POST SYNTHESIS RAPID THERMAL ANNEALING
AND CHARACTERIZATION OF COLLOIDAL
NANOPARTICLES

By

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Abstract

Post Synthesis Rapid Thermal Annealing and Characterization of Colloidal Nanoparticles

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This Masters thesis investigates the effects of post growth rapid thermal annealing on colloidal CdTe nanoparticles. This novel process has not previously been applied to colloidal nanoparticles. It is found that rapid thermally annealing with temperatures up to 400°C, the number of defect bonds in the semiconductor core will decrease and the zincblende structural phase will prevail. These findings are identified using Raman spectroscopy enhanced in a liquid core waveguide and corroborated using a variety of other analysis techniques. What is also important is that while the semiconductor core is changing, the optical characteristics of the material remain nominally unchanged. Additionally, a circulatory peristaltic pump system that is suitable for future in situ monitoring was developed and used to investigate the length effects of Teflon capillary tubes as a liquid core waveguide for Raman spectroscopy.
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List of Acronyms

NP - Nanoparticle
QD – Quantum dot
LED – Light emitting diode
QD-LED – Quantum dot – Light emitting diode
PL - Photoluminescence
UV-vis – UV-visible spectroscopy
XRD – X-Ray diffraction
TEM – Transmission electron microscopy
HRTEM – High resolution transmission electron microscopy
LCW – Liquid core waveguide
RTA – Rapid thermal annealing
XPS – X-Ray photoelectron spectroscopy
CCD – Charge coupled device
LIRS – Laser injection rejection system
NA – Numerical Aperture
TCT – Teflon capillary tube
HC-PCF – Hollow core – photonic crystal fiber
PAA – Polyacrylic acid
TIR – Total internal reflection
Chapter 1. Introduction

Semiconductor nanoparticles (NPs) of numerous shapes, sizes, and compositions have emerged over the past two decades that exhibit exciting material, optical, and electrical characteristics.\(^1\)\(^-\)\(^4\) NPs are commonly referred to as quantum dots (QDs) and are defined as a semiconductor crystalline cluster that has its physical dimensions constrained to several to tens or perhaps hundreds of nanometers. On this size scale, the semiconductor particle contains anywhere from several hundred up to tens of thousands of atoms. At this size scale, quantum size effects take control in contrast with bulk materials of similar variety. This quantum size effect allows for the adaptation of optical and electrical properties of semiconductors simply through control over the size and shape of the nanocrystal. The characteristic of quantum dots to have changing material properties simply due to the size of the NPs offers exciting possibilities from biological imaging applications, novel optical devices, to quantum communications and computing. While the theoretical motivation for utilizing these QDs has been presented, reliably synthesizing useful NPs is not an elementary task. There are a variety of methods to create semiconductor NPs with the three most common being\(^5\):

1. **Epitaxial Growth**-
   
   Epitaxial growth of QDs involves the growth of clusters of material on a substrate. Growing epitaxial dots is accomplished through the borrowing of different thin film techniques such as molecular beam epitaxy, chemical vapor deposition, or laser ablation. Epitaxial quantum dots are spontaneously formed three dimensional islands by strained-layer heteroepitaxy.\(^6\) The mismatch of surface free energies and lattice spacing between the substrate
and deposition material creates abnormal strain on the material being deposited. As such, the total strain is reduced by the formation of coherent islands since the elastic relaxation at the free edges of the islands counteracts the additional surface energy that would be introduced to the system if a homogeneous film had formed instead.\textsuperscript{7} It is the nature of the materials to minimize the strain between the substrate and deposition layers that results in small islands of growth (the QDs) on the substrate rather than a homogeneous film. Variations in QD size and number density can be tuned through changes in lattice mismatch, material composition, growth kinetics, and substrate roughening.\textsuperscript{8} The promise of epitaxial growth of QDs is that the processing methods are already developed and in use for the thin film and semiconductor industry. As well, the growth mechanics inherently create nearly uniform size distribution since the larger islands under higher strain grow more slowly than the smaller islands.\textsuperscript{8} However, problems with epitaxial growth of creating NPs include throughput, adaptability, and cost.

2. **Ion Implantation**

Ion implantation involves bombarding a desired substrate with specific types of high-energy ions.\textsuperscript{9} These ions become embedded in the substrate, which subsequently acts as a matrix to contain the QDs. Following implantation, the material is annealed at sufficiently high temperatures to allow the diffusion of the implanted ions yet low enough to conserve solution oversaturation.\textsuperscript{10} The annealing process can be split into three separate phases: nucleation, growth on account of dissolved matter, growth on account of recondensation.\textsuperscript{10} The
initial annealing causes nucleation of the ions into minimally sized quantum particles that act as nuclei for further growth. Following the appearance of these nuclei, the annealing then promotes additional material to grow onto the nuclei. During this step, the size of the individual particles increases, but the overall number of entities remains unchanged. Finally, the annealing, and growth process is completed by the dissolution of the smaller nanoparticles into the larger ones during the recondensation phase.\textsuperscript{10} Annealing often takes place at high temperatures and thus only select materials are suitable for this method. Specific characteristics of the QDs can be adjusted by changing the semiconductor material, lattice structure, concentration of the implanted ions, and annealing settings. Ion implantation allows for the wider growth of various QD semiconductors in a variety of substrates.\textsuperscript{10} Again, throughput and cost can pose additional problems, since the growth techniques used are based on current semiconductor technologies.

3. \textit{Colloidal Growth-}

Colloidal growth, in comparison to the previous substrate reliant methods is based on wet chemistry synthesis. In fact, the development of colloidal NPs can be thought of as a type of macromolecule with a similar growth procedure as those utilized for organic polymers.\textsuperscript{11} In this method, it is typical for three different types of components to be used: precursors, organic surfactants, and solvents. Initially, the precursors are mixed in with the solvent and heated to a sufficient temperature at which the precursors react to create a supersaturation of monomers followed by the nucleation of nanocrystal ‘seeds’.\textsuperscript{11} With time,
additional monomers are deposited onto these nuclei resulting in further
growth of the particles. In a similar manner to the recondensation growth
from ion implantation, many colloidal nanocrystal systems undergo Ostwald
ripening in which the smaller particles, due to their high surface energy are
dissolved and redeposited on the larger crystals.\textsuperscript{5} In order to arrest further
growth of these NPs into larger particles not governed by the quantum size
effect and also to stabilize the crystals, the ripening process is halted by
introducing a surfactant such as an organic ligand or polymer. Following the
NP growth a precipitation step is often performed whereby a poor solvent for
the NPs is introduced to the stable solution that acts to reduce the solvating
power of the main solvent. Subsequently, the larger NPs will precipitate out
of solution first due to their larger van der Waals forces, and then through
careful titration a narrowing of the size distribution can be obtained.\textsuperscript{5,11}
Provided the growth recipe and procedure has been properly developed and
carried out, the final product will be a monodisperse solution of stable
semiconductor NPs surrounded by a capping organic.

Colloidal NPs can offer significant advantages in comparison to other methods of
synthesis such as:

1. \textit{Cost-}

Wet chemical synthesis uses materials and equipment found in common
chemistry labs. This eliminates the requirement for expensive equipment
common in the semiconductor industry to process wafers and grow NPs upon
them. In addition, whereas the throughput of epitaxial and ion implanted NPs relies on the volume and speed capabilities of the growth equipment, colloidal NPs can be made in large quantities simply by scaling up the amount of reactants used.

2. Mobility-

Colloidal NPs are inherently free moving in solution. In epitaxial growth or ion implantation, a major drawback is that QDs are fastened onto a specific structure and in a specific order dependent on the growth mechanisms. Conversely, colloidal growth can facilitate the transfer of the QDs to any structure or area that the NP solution has access to. This offers more options in terms of reorganizing or relocating the NPs into a different matrix, onto a different surface, or into complex structures.

3. Flexibility-

The characteristics of wet chemical synthesis in a mobile platform, contribute to making the overall system very flexible in terms of adaptability. There are currently many different types of colloidal NPs that differ in terms of core material, capping layer, size, and shape. With such variety, these NPs are being investigated for use in wide ranges of applications involving implementation into a plethora of structures, solvents, and surfaces.

With the advantages that colloidal NPs have in comparison to other growth techniques, potential applications are extremely widespread. Initially, colloidal QDs were identified as being a potential material for targeted biological imaging as a
replacement of fluorescent organic dyes.\textsuperscript{12,13} This is primarily due to the compatibility of water soluble NPs with biological systems. However, the realm of uses for colloidal NPs is continually expanding and now includes areas such as light emitting diodes (LEDs),\textsuperscript{14} efficient solar cells,\textsuperscript{15} ultrafast electron transfer,\textsuperscript{16} and negative refractive index materials.\textsuperscript{17}

Specifically, CdTe QDs are of particular interest to a number of biomedical, optoelectronic, and photovoltaic applications. It has previously been shown that by adjusting the radius of colloidal CdTe QDs from approximately 4.5 nm to 1.75 nm, the energy gap has been measured to range from around 1.65eV to 2.2eV respectively.\textsuperscript{18} With easily tunable band gaps, semiconductor QDs are touted to be highly influential in biological detection probes. Employing CdTe QDs in biological detection delivers a number of advantages over the traditional method of using organic dyes. These advantages include a high quantum yield, high molar extinction coefficient, broad absorption with narrow, symmetric photoluminescence, a high range of tunable spectra, high resistance to photobleaching, and improved resistance to photo or chemical degradation.\textsuperscript{19} Colloidal CdSe was highlighted in 1998 as the first semiconductor to be used for biological detection, and has been involved in most research over the past decade. However, CdTe is expected to prove itself an exciting alternative to overcome the more complicated, time consuming, and expensive method of creating CdSe QDs. In addition to simplified synthesis techniques, CdTe QDs are advantageous due to their ability to be directly grown in water unlike CdSe.\textsuperscript{19} CdTe nanocrystals also have potential in creating increased efficiency photovoltaic (PV) cells.\textsuperscript{20} Adjusting the central wavelength of a PV cell becomes simplified and various wavelengths of detection can be
optimized for using the same basic materials and process. Again, other semiconductors such as PbSe and CdSe can also be used to create these QDs. Compared to CdSe, CdTe has a lower bulk band gap energy that enables it to cover a larger portion of the solar radiation spectrum. CdTe inherently offers a higher electron mobility value compared to CdSe, which should theoretically result in higher solar cell efficiencies. While PbSe demonstrates a stronger quantum confinement, the band gap is only tunable from 0.5eV to 1.6eV for QD radii of 4.5 to 1.5 nm respectively. This energy range, while encompassing the infrared energies emitted by the sun, does not reach across the visible spectrum, which is desirable for other PV sensor applications. CdTe NPs also hold an exclusive advantage in terms of obtaining NP samples and material support. The company Vive Nano Inc. is a spin-off company from the University of Toronto Department of Chemistry, and they manufacture CdTe colloidal QDs capped with polyacrylic acid (PAA). While it is acknowledged, that PAA is an insulating polymer and not optimum for carrier transport applications, the demonstration of certain processing techniques on this system can act as a proof of concept for future fully implemented devices. In addition to having a close working relationship with the University of Toronto, Vive Nano Inc. is interested in investigating other product characterization methods and post synthesis adaptations of their products.

1.1- Nanoparticle Characterization

In order to tune characteristics of colloidal NPs for specific applications, precise methods of analysis must be implemented to characterize and analyze various types of NPs. There is a variety of different methods being employed to study the properties of
semiconductor NPs. A more detailed investigation of characterization methods applied for this thesis will be covered in Chapter 3, however, some of the most common analysis methods, but certainly not an exhaustive list include:¹

1. **Photoluminescence**

   Photoluminescence (PL) is an optical method of analyzing the electronic states of the NP. It involves optically exciting the QDs, often using UV light, and then capturing the re-emission of the absorbed photons. As the emitted light is directly dependent on allowed energy levels, it is a simple method of probing the electronic states within the material. PL can also be expanded to detect the specific mechanisms of the re-emission (for example whether the radiation is dominated by band-edge recombination or trapped state recombination) through time-resolved analysis. ²³

2. **Ultraviolet-visible Absorption Spectroscopy**

   Ultraviolet-visible (UV-vis) absorption is another optical means of analysis that is often used as a complement to PL. Rather than collect the emitted light from the NPs, instead, the remainder of light that has passed through the NP solution is gathered and analyzed. With this information, the level of absorption of different wavelengths of light by the material can be analyzed. Both PL and UV-vis aid in the investigation of size effects on the energy levels present in the QDs. ²⁴

3. **X-Ray Diffraction**

   X-Ray diffraction (XRD) involves a collimated X-Ray beam being focused on the material. The rays are then diffracted according to the present crystalline phases in the sample and collected upon incidence with the material. XRD has been used to determine
different crystalline structures present in NPs, and can potentially be utilized to determine unknown substances, NP size, and chemical composition in QD materials.$^{25,31}$

4. *Transmission Electron Microscopy*

Transmission electron microscopy (TEM) is a method of obtaining an actual picture of the QDs themselves. Using a beam of electrons to pass through a portion of the material an image can be collected based on the interaction of the beam with the particles. This method can be even further improved upon using high resolution TEM (HRTEM), to focus on and image a single colloid NP.

However, despite the aforementioned analysis methods and a plethora of others that were not mentioned, there are problems with many current methods ranging from processing time to prepare the sample for characterization such as with TEM, destruction of the material with XRD, to limited useful information with PL. In addition, none of the currently available methods are suitable for real-time in situ monitoring during the growth process of the NPs. Obtaining an adequate method of analysis that could provide certain desired information in situ would be particularly valuable. Raman spectroscopy is a non-destructive, optical method of analysis that probes the vibrational modes allowed in the material. Raman has been used extensively in other material analysis systems but has had limited use thus far in the characterization of colloid NPs in solution due to the inherently weak Raman mechanism that is worsened further if the sample is a dilute solution. As shall be covered in the next chapter, the signal from a dilute sample can be greatly enhanced if it is placed within a liquid core waveguide (LCW), enhancing the sensitivity of the characterization technique.
1.2- *Post-Synthesis Processing of Nanoparticles*

While a long term goal of Raman spectroscopy using LCWs may be in situ analysis during the NP synthesis procedure, there is currently no implemented method of such control. Depending on the end use of the NPs, whether it be for QD-LEDs, solar cell applications, or biological imaging, different types and characteristics (for example color, crystallinity, or capping material) of NPs may be required. Obtaining NPs with varying characteristics through the growth procedure can often be a difficult and time consuming process to determine exactly what changes in the synthesis process affect what characteristics. Rather, a much more economically feasible method of synthesis would be to create one large batch of NPs and then selectively process certain portions of the sample for different applications. As such, exploring different methods of post-synthesis processing of NPs to identify beneficial changes is important. As well, it is additionally important to explore the effects of current semiconductor processing techniques that are utilized in industry. In order to efficiently implement colloidal QDs into current semiconductor technologies, the effects of commonly used manufacturing techniques on NPs also needs to be explored in order to determine compatibility. Two examples of post-synthesis processing of semiconductor NPs that have been investigated include:

1. *Ligand Exchange*

NPs can currently be designed to be soluble in a number of different solvents with a variety of types of ligands surrounding the core and providing quantum confinement. However, different applications may require different types of capping ligands that are not compatible with the current synthesis processes. As
such, post growth ligand exchange can be performed to change the capping layer of the NP. This ligand exchange has been shown to have effects on solubility, photoluminescence, and trapped surface states in the NP.\textsuperscript{26,27}

2. \textit{Post growth annealing}

NPs can also be annealed post synthesis to influence changes in the NPs. Studies have shown significant changes in the fluorescent output of the NPs with both relatively low temperature (sub 200°C annealing) and also high temperature (700-900°C annealing) conventional annealing.\textsuperscript{22,28} Both the fluorescent intensity and also the output wavelength can be affected by an annealing process.

The technology to be utilized in this thesis is rapid thermal annealing (RTA). RTA is a technique used in semiconductor and polymer processing in which the traditional annealing process is highly accelerated, while still maintaining an isothermal process.\textsuperscript{29} The goal of this method is to influence specific material change in the material while at the same time preventing detrimental drawbacks that would otherwise take place with longer anneal times. This technique has already proved to be beneficial in repairing crystal defects in semiconductors that were introduced by ion implantation and also large volume roll-to-roll processing in polymer based solar cells.\textsuperscript{29,30} Applying this novel processing technique on NPs has not before been investigated, and using it to influence desirable changes would offer an additional processing technique for NP research and implementation into optoelectronic devices.
1.3- Thesis Objective

The ultimate goal of this thesis is twofold. It is to apply the post synthesis process of RTA to semiconductor NPs, which has not previously been performed on such material. Subsequent to the processing, characterization of the processed semiconductor NPs in their liquid form will be performed utilizing Raman spectroscopy combined with a LCW. The aim of this processing is to transfer some of the advantages that RTA has demonstrated beneficial from the semiconductor industry into the CdTe NP material. While PL, is a standard in optical characterization of NPs, it does not provide any further information aside from the electronic states. Rather, Raman spectroscopy has been shown to provide much more in depth analysis of the structure of materials. Using Raman spectroscopy in conjunction with LCWs has been successful in providing greatly enhanced sensitivity, and it is a goal to use this characterization technique to probe the changes occurring at the nanometer scale in these NPs. Since this characterization method is novel and relatively undocumented when used on semiconductor NPs, additional methods of analysis will be performed including UV-Vis, XRD, XPS, and TEM, to corroborate the results of the Raman spectroscopy and more completely explain the phenomena occurring within the NP material due to the application of RTA. In addition, to continually approach the ultimate goal of in situ monitoring using Raman spectroscopy the development of sample circulation through the LCW and investigation into the optimum length of LCW for the Raman signal produced will be explored theoretically and experimentally.
Chapter 2.  Raman Spectroscopy

Raman spectroscopy is a non-destructive, optical method of material analysis. Characteristics of a sample are obtained by analyzing monochromatic light that has undergone inelastic scattering upon interaction with the sample. Raman scattering was first observed in 1928 by Venkata Raman. In general, there are three possible outcomes that may occur when light is incident on matter: the light may be absorbed, scattered, or have no interaction at all. If the light interacts with a material and is not absorbed, it is considered scattered. There are additionally, two main classifications of scattering. If a monochromatic radiation of given frequency \( \omega_0 \) is incident on a surface and is elastically scattered without any change of frequency, it is classified as Rayleigh scattering, whereas if the scattering is inelastic and the collected light contains a different frequency, it is referred to as having been Raman scattered.

2.1- Macroscopic Theory of Raman Scattering

The Raman scattering phenomenon can be understood on a macroscopic level using postulates based on classical mechanics. When an electromagnetic wave with an electric field of \( E \), is incident on a medium, it will induce a polarization \( P \), in the material. \( E \) is a sinusoidal plane wave of the form

\[
E = E_0 \cos(2\pi v_it)
\]  

(2.1)

where \( E_0 \) is the complex amplitude and \( v_i \) is the frequency. The polarization induced is defined by

\[
P = \alpha E
\]  

(2.2)
where \( \alpha \) is the polarizability of the material. \( \alpha \) in turn is a tensor and is a function of the nuclear coordinates and atomic displacements. Any material above absolute zero will have thermally excited atomic vibrations causing the polarizability to fluctuate. \( \alpha \) can thus be expanded into a Taylor series dependent on the plane wave \( Q \), which are the normal modes of atomic vibrations permitted in a crystalline semiconductor. \( \alpha \) is defined as

\[
\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q + \ldots
\]  

(2.3)

where the subscript ‘0’ designates the values and derivatives at the equilibrium position of the system. \( Q \) takes the known form of a plane wave and is defined as

\[
Q = Q_0 \cos(2\pi v_{\text{vib}} t)
\]  

(2.4)

where \( v_{\text{vib}} \) is the frequency of the normal mode vibration in the semiconductor.

Substituting equations (2.1), (2.3), and (2.4) into equation (2.2), gives a result of the form

\[
P = P_0 + P_{\text{ind}}
\]  

(2.5)

where the term \( P_0 \) is equal to

\[
P_0 = \alpha_0 E_0 \cos(2\pi v_{\text{vib}} t)
\]  

(2.6)

and is a polarizing vibration with the same frequency and phase as the incident radiation.

The second term, \( P_{\text{ind}} \) is defined by

\[
P_{\text{ind}} = \frac{E_0}{2} \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q \cdot \left\{ \cos[2\pi (v_f + v_{\text{vib}}) t] + \cos[2\pi (v_f - v_{\text{vib}}) t] \right\}
\]  

(2.7)

As can be seen in (2.7), this polarization contains two sinusoidal waves with slightly shifted frequencies from the incident wave dependent on the allowed vibrations in the crystal structure. The term containing a decrease in frequency \( (v_f - v_{\text{vib}}) \) is considered an increase in frequency \( (v_f + v_{\text{vib}}) \) is considered
anti-Stokes shifted. Equation (2.5) describes both the polarization of the material and subsequent Rayleigh and Raman scattering of light from the crystal. While it may not be obvious simply from the derivation given, the \( P_0 \) term of the polarization is much stronger than the \( P_{\text{ind}} \) term. In addition to this first order Raman scattering, the Taylor series from equation (2.3) can be expanded to include higher order terms that results in higher ordered Raman scattering.

2.2- *Microscopic Theory of Raman Scattering*

While the Raman scattering effect has been derived classically in the previous section, it cannot adequately explain the complete phenomenon. Raman scattering can be rigorously derived using quantum mechanics, however, it is often understood using a quasi-quantum mechanical model known as the energy transfer model.\(^{33}\)

In order to adequately describe the scattering mechanisms using the energy transfer model, some quantum mechanical definitions are required. The first is the definition of a photon. A photon is the basic unit of electromagnetic radiation. It can be thought of as a quantum or “particle” of light that has energy

\[
E = h\nu
\]

(2.8)

where \( h \) is Planck’s constant and \( \nu \) is the frequency of the light.

In addition, a related concept that is particularly relevant to crystallized semiconductors is that of a phonon. In a corollary to the way that a photon is a quantum of electromagnetic radiation, a phonon is a quantum of atomic vibration of the normal modes allowed in a lattice. A phonon can be defined as having energy

\[
E = h\nu_{\text{vib}}
\]

(2.9)

where \( \nu_{\text{vib}} \) the frequency of the normal mode in the lattice.
As was explained previously, when a light beam encounters a material, a portion of the photons that comprise the radiation will be scattered, but only one in approximately $10^6 - 10^8$ scattering events is of the Raman variety. All scattering interactions must conserve both energy and momentum. An inelastic Raman scattering event is one in which the incident photon indirectly interacts with a phonon in the crystal lattice of the sample to scatter the photon with a frequency slightly different from that of the incident photon. If the scattered photon has a lesser frequency (less energy) than the incident one, it is considered Stokes scattered, and conversely if the scattered photon has a higher frequency (more energy) it is classified as anti-Stokes scattered. Figure 2-1 is an energy level diagram depicting in a), elastic Rayleigh scattering, in b), inelastic Stokes scattering, and in c) inelastic anti-Stokes scattering.

Figure 2-1: Energy level diagrams of the different scattering processes that can occur upon the interaction of light with matter.

Intuitively it may be thought that the photon directly interacts with the phonons in the crystal, however, this is not the case as the probability of this interaction is extremely small unless the photons and phonons have comparable frequency. Rather, the incoming photons effectively only couple to electrons, which in turn interact with the
phonons in the system. As the incident photon interacts with the atoms of the sample, it temporarily excites an electron in the semiconductor material to an unstable virtual state creating an electron-hole pair. This virtual state is not a solution of the time-independent Schrödinger equation for the material and this process is termed virtual absorption. The excited electron-hole pair quickly recombines, bringing the system back down to a ground state and emitting a photon. Most often, the initial and final states of the system are the same resulting in a photon of the same frequency as was virtually absorbed to be emitted. However, the electron-hole pair can be scattered by a phonon into another state via electron-phonon interaction Hamiltonian before recombining and emitting radiation. The end effect is the same as is depicted in Figure 2-1, in which the incoming photon can be scattered either at the same frequency with which it had prior to the interaction, or at a slightly shifted one.

It should be noted that Raman scattering does not necessarily require an ordered lattice with allowed phonon modes, as certain molecular vibrations in non-crystalline materials can and will interact in a similar manner to the aforementioned phonon interactions.

2.3- **Raman Spectrometer Setup**

The Raman spectroscopy system being used for measurements is the LabRam HR 800 manufactured by Horiba Jobin Yvon. The key system components are:

- an internal HeNe 20 mW laser operating at 633 nm
- a notch filter designed to filter out the excitation wavelength with <120 cm\(^{-1}\)

Stokes edge

- an adjustable confocal hole between 0 and 1108 µm
- air cooled 1024x256 silicon CCD detector
- density filter wheel with filters D0.3, D0.6, D1, D2, D3, and D4
- an asymmetric Czerny Turner spectrograph with two gratings: 1800 l/mm and 600 l/mm
- choice of three objective lenses (Olympus M PLAN, 10X, 50X, and 100X)
- high quality color camera for microscope

Shown in Figure 2-2 is the basic schematic and beam path for a standard Raman measurement.

![Figure 2-2: Schematic of the LabRam HR 800 Raman spectrometer.](image)

In a typical Raman measurement, the laser light is directed onto the sample by a series of reflections from mirrors and is focused appropriately using the internal lenses. Prior to interacting with the sample, the laser passes through a density filter wheel. The power of the laser will then be reduced from the initial 20 mW depending on the filter.
The laser power is reduced according to the formula

\[ P_N = \frac{P_0}{10^{OD}} \]  

Where \( P_N \) is the power after the filter, \( P_0 \) is the power before the filter, and \( OD \) is the optical density of the filter chosen. As was identified previously, the optical densities of the filters available with the system range from 0.3 to 4.

The angled mirror and notch filter labeled in Figure 2-2 is given the term laser injection rejection system (LIRS). This system acts to allow the notch filter to completely reflect the incoming laser beam onto the sample as long as it is incident at an appropriate angle. Lens 1 subsequently produces a parallel beam that is then focused onto the sample by the objective lens. The system operates in a backscattering geometry, in the sense that the scattered radiation from the sample is collected by the same objective lens that is used to focus the sample. This scattered radiation then travels back through the system, but the LIRS acts to now pass any radiation that was not Rayleigh scattered through the notch filter. The system is designed such that the image of the Raman beam is focused by Lens 1 onto the confocal hole. Due a mismatch in the length of Lens 1 and the tube length of the objective lens, the image of the sample is magnified by 0.2x Objective lens used onto the confocal hole. Not pictured in Figure 2-2 is a second notch filter located immediately before the confocal hole that further removes Rayleigh scattered light, and allows Raman signal to be analyzed that has wavenumbers less than 120 cm\(^{-1}\). Lenses 2 and 3 then projects the light that passes through the confocal hole onto the entrance slit to the spectrograph and at the same time reduces the image of the confocal hole by a factor of five.
As the beam passes into the spectrograph, it encounters a spherical mirror with an 800 mm focal length. This mirror works to change the previously diverging beam into one of parallel nature. This parallel beam is directed onto a diffraction grating (either 1800 l/mm or 600 l/mm with this system) before being collected by a complementary spherical mirror also with an 800 mm focal length and focusing the diffracted beam onto the CCD camera.

2.4- Factors Affecting the Raman Signal

Due to the weak interaction inherent to Raman scattering in dilute solutions, it is important to investigate and optimize the Raman signal coming from the liquid NP samples. In order to do this it is vital to understand what contributes to the intensity of the Raman signal. A concept vital to the intensity of the Raman scattering from a sample is that of Raman cross section. The Raman cross section, $\sigma$, is a parameter that is used to describe the probability of an incident photon being Raman scattered by a particular phonon or vibration. Using the classical treatment of Raman scattering, the rate of Raman scattered photons ($P_R$) in photons/s can be defined as

$$P_R = P_0 \sigma D dz$$

(2.11)

where $P_0$ is the incoming rate of photons (photons/s), $\sigma$ is the Raman cross section (cm$^2$/molecule), $D$ is the density of scattering centers (molecules/cm$^3$), and $dz$ is the path length of the laser in the sample. In practice however, it is much more common to define a differential cross section, $\beta$, that is defined as

$$\beta = d\sigma / d\Omega$$

(2.12)
where $\Omega$ represents the solid angle of collection. The reasoning behind this definition is due to the requirement that to realize the total number of Raman scattered photons ($N_R$) would require collection of scattered light over all $4\pi$ steradians around the scattering centers. In laboratory measurements, only a small portion of the total scattered radiation is actually collected, thus using $\beta$ with units of (cm$^2$sr$^{-1}$/molecule) is much more applicable. Therefore, from equations (2.11) and (2.12) we can now create the overall expression for

$$dP_R / d\Omega = P_0 \beta D dz$$

(2.13)

defining the rate of Raman scattered photons in a steradian of collection angle. Moving one step further and referring to the laser in terms of power density per steradian ($I_R$) in units of (photons/s sr$^{-1}$ cm$^2$) rather than total power gives:

$$I_R = I_0 \beta D dz$$

(2.14)

Where $I_0$ (photons/s cm$^2$) is now the irradiance of the incident beam on the sample. Defining the Raman signal as collected by the spectrograph and measured by the CCD, $S_R$, expressed in number of electrons is defined as

$$S_R = I_R C_t s = I_0 \beta D dz C_t s$$

(2.15)

where $C$ is a collection function that is dependent on the collection and detection characteristics of the Raman spectrometer. This function can be broken down further as follows:

$$C = A_D \Omega_D T Q$$

(2.16)

Where $A_D$ is the area the spectrometer and optics can monitor, $\Omega_D$ is the solid angle in steradians collected by the spectrometer, $T$ is the losses associated with the optics (filters and lenses) in the system, and $Q$ is the quantum efficiency (electron/photon) of the
detector being used. It should be noted that $\Omega_D$ is directly dependent on the numerical aperture (NA) objective lens used to image the sample. While for low NA values (less than 0.5) an approximation can be made that

$$\Omega_D = \pi NA^2$$  \hspace{1cm} (2.17)

Since the NA range of the objectives on the LabRam HR 800 range from 0.1 to 0.9, it is more accurate to use the definition

$$\Omega_D = 2\pi \{1 - \cos[\sin^{-1}(NA)]\}$$  \hspace{1cm} (2.18)

Raman spectrometers can operate in two different methods depending on the collection characteristics as defined by the confocal hole, entrance slit, and magnification system. These two variations are termed “underfilled” and “overfilled” and pictorial examples of each mode are shown in Figure 2-1.

**Figure 2-3:** Comparison of “underfilled” and “overfilled” Raman collection methods.
As is evident, in the “overfilled” case, the detected area is smaller than the illuminated region of the sample by the laser beam, so the total amount of Raman scattering within the signal is not being detected. Alternatively, in the “underfilled” case, the total laser spot on the sample is being collected and the entire region emitting Raman scattered radiation can enter the spectrograph. While with a traditional solid sample, the LabRam HR800 will always be operating in “underfilled” mode, combining Raman spectroscopy with LCWs the collection mode can change depending on the size of the LCW core and the spectrometer settings. Depending on the collection mode, the final equation governing collected Raman signal can change. In general, combining equations (2.15), (2.16) and (2.18), and converting the incident irradiance into a more general power per area, an overall expression for Raman signal in electrons from a sample can be defined as:

\[
S = P_0Bdz\frac{A_D}{A_L}2\pi\{1 - \cos[\sin^{-1}(NA)]\}QT_s, \quad (2.19)
\]

This formula can be slightly simplified if the spectrometer is operating in “underfilled” since the detection area and laser spot area can be equated to each other if it is assumed that no Raman signal is coming from outside of the illumination area of the laser. From this final equation, a variety of adjustments can be identified in attempts to enhance the weak Raman signal coming from the sample. The most applicable of which to this thesis is the combination of \(\beta\) and \(dz\). While not explicitly derived, the differential scattering cross section \(\beta\) has units of \(\text{cm}^2\text{sr}^{-1}/\text{molecule}\). When multiplying this with \(dz\),
the subsequent term has units of $\text{cm}^3\text{sr}^{-1}$/molecule and is dependent on the scattering volume of the sample.

2.5- Raman Spectroscopy of Liquid Samples using Liquid Core Waveguides

The use of LCWs with liquid samples effectively increases the scattering volume of the Raman scan. It has been shown experimentally that the use of waveguides both Teflon capillary tubes (TCTs) and hollow core photonic crystal fibers (HC-PCFs) significantly enhances the Raman signal of the sample being investigated.\textsuperscript{36-38} Figure 2-4 shows a schematic of the LCW being used for waveguiding.

Figure 2-4: Schematic diagram of a LCW as a waveguide.
The Raman power (W) being emitted from the end of the waveguide can be
determined through the equation

\[ P_R = L_R G \]  
\[ (2.20) \]

where \( L_R \) is the radiance in \( (W \ m^2 \ sr^{-1}) \) and \( G \) is the optical conductance of the system
\( (m^2 \ sr) \). The optical conductance of a radiating (or being radiated on) component is

\[ G = n^2 A \Omega \]  
\[ (2.21) \]

where \( n \) is the refractive index of the surrounding material, \( A \) is the area of the radiating
system, and \( \Omega \) is the solid angle of radiation. Assuming the small angle approximation
and that the interface between the liquid and air is completely flat, the Raman signal
being emitted from the end of the waveguide would be emitted in a cone with angle \( \phi \) as
depicted in Figure 2-4, where

\[ \phi = \sin^{-1} \sqrt{(n_{co}^2 - n_{cl}^2)} \]  
\[ (2.22) \]

where \( n_{co} \) is the refractive index of the core and \( n_{cl} \) is the refractive index of the cladding.

Holding to the aforementioned assumptions, the solid angle subtended by the light from
the LCW can be approximated in steradians as

\[ \Omega \equiv \pi NA^2 = \pi (n_{co}^2 - n_{cl}^2) \]  
\[ (2.23) \]

From theoretical investigations by Altkorn et al.\(^{39}\) the Raman radiance \( (W \ sr^{-1} \ m^2) \) at a
circular face, \( L_{int} \), within the LCW can be defined as

\[ L_{int} = \frac{P_L s}{\pi r^2} \Delta z \]  
\[ (2.24) \]

where \( P_L \) is the pump laser power, \( r \) is the radius of the core of the LCW, \( \Delta z \) is the
illuminated LCW length and \( s \) is the Raman scattering coefficient in \( (sr^{-1} \ cm^{-1}) \). It should
be noted that while \( s \) is related to the previously defined scattering coefficient \( \beta \), it is
defined slightly differently. Regardless, the basis is the same, in that the scattering coefficient is a measure of the probability for the incident light to be Raman scattered from the sample. However, since the irradiance that is of interest to the system is that outside the sample liquid, it can be shown, again using the small angle approximation, that the irradiance across the end face decreases by a factor of $1/n_{co}^2$, as the Raman light refracts across the sample-air boundary. Therefore, combining this fact into Equation (2.24), and substituting Equations (2.24), (2.23), and (2.21) into Equation (2.20), the total Raman power exiting the waveguide can be derived as:

$$P_R = \frac{P_L s\pi (n_{co}^2 - n_{cl}^2)}{n_{co}^2} z$$  \hspace{1cm} (2.25)$$

where $z$ is the length of the LCW rather than an infinitesimally small slice.

Equation (2.25) however, makes the assumption that the LCW is short enough that there is no attenuation of either the pump power or the Raman scattered signal along the length of the waveguide. Instead, an effective value of the LCW length ($z_e$) can replace the length, $z$, in Equation (2.25). This effective length is dependent both on the geometry of the Raman collection and the attenuation from in the LCW itself. In the case of a backscattered geometry, the effective length is defined as

$$z_e = \frac{(1 - e^{-2\alpha z})}{2\alpha}$$  \hspace{1cm} (2.26)$$

where $\alpha$ is the attenuation in the fiber.

From the discussion and equations in the previous section, the benefit of combining LCWs with in the enhancement of Raman signal from dilute liquid samples is apparent.
Chapter 3. Experimental Details

3.1- Rapid Thermal Annealing

RTA is a processing technique akin to conventional oven annealing with one significant difference. As the name might suggest, the annealing process is greatly accelerated with RTA. Whereas a conventional anneal can take hours to complete, RTA processes typically only take on the order of tens of seconds to complete. This reduction of time spent at high temperatures can be critical to samples that need a very low thermal budget. The term thermal budget refers to the total amount of thermal energy that is transferred to a sample during processing. A low thermal budget is desired for many current semiconductor technologies in order to limit dopant impurity diffusion and oxide growth. This is becoming all the more important as the physical dimensions of integrated circuits are becoming exceedingly smaller. At the same time, achieving high temperatures is required in order to activate desired phenomena in the same samples. The use of RTA permits samples to be annealed at high temperatures, but due to the limited time of the process, the thermal budget of the anneal can be kept low. RTA has been applied successfully in the semiconductor industry to create ion implanted junctions, remove defects from ion implantation without excessive dopant diffusion, and also in thin film deposition or growth. There are other rapid heating processes that also have a reduced thermal budget that primarily rely on the use of lasers to transfer heat to the sample. Shown in Figure 3-1 is a comparison of three different methods of heating processes that limit the thermal budget to the sample. Adiabatic rapid processing is often performed by a high powered laser beam being focused on the sample for times less than
$10^{-6}$ seconds. As can be seen, the heating does not penetrate deeply into the sample and often can result in the melting of the surface of the sample due to extreme heat at the focus point. The second method, thermal flux processing, is often achieved by the scanning of lasers or electron beams across the surface of the sample. Typical process times are on the order of $10^4$ seconds. From the temperature-depth profile, it is obvious that while the temperature penetrates further into sample, it does not do so uniformly, and as such, the thermal effects are not constant throughout the material. However, in the isothermal case (which is equivalent to the RTA process being used in this thesis), the sample is heated by defocused, incoherent light, often from tungsten halogen lamps or arc lamps. In this process, the radiation is subject on the material uniformly and penetrates throughout the sample providing a uniform temperature – depth profile desired.

![Figure 3-1: Schematic of three rapid heating processes with the temperature depth profiles shown beside them. Taken from Singh [29].](image-url)
While RTA has been applied extensively to semiconductor systems, it has not been thoroughly explored with respect to NP materials. Conventional post synthesis annealing has been applied to NPs with varying effects on the NP characteristics. Most notably, these processes have been shown to provide structural and contact benefits in LED structures, while at the same time, due to the high thermal budget, diminishing the photoluminescence (PL) efficiencies at temperatures below 200°C. This is due to the fact that while the quantum size effects of the NPs control the optical characteristics of the emission wavelength, the actual recombination of charge carriers resulting in light emission is primarily dominated by trapped carrier states created on the interface between the inorganic core and the capping material. Thus, when annealing takes place for relatively long amounts of time, the capping polymer is allowed to readjust, and reconfigure itself along the surface, altering the high density of surface trap states available. The NPs used in this thesis are capped with polyacrylic acid (PAA), which has a glass transition temperature of 106°C. Above this temperature, the polymer chains in the capping material become mobile allowing significant reorganization at the NP interface and potential loss of trapped surface states. However, in order to influence the semiconductor core of the NPs, temperatures in excess of the glass transition temperature are required. Thus, to maintain both the attractive optical properties of the NPs, while at the same time influencing the core of the NP, the amount of time spent above the glass transition temperature of PAA should be limited. As has been discussed, this can be achieved through the RTA procedure.
3.1.1- Rapid Thermal Annealing Configuration

The equipment used for the RTA process was the *AnnealSys AS-ONE Rapid Thermal Processing Furnace.* This system can anneal at a temperature range from room temperature up to 120°C at a maximum heating rate of 200°C/s. It has gas-mixing capabilities with mass flow controllers and a vacuum range from normal atmospheric pressure down to $10^{-6}$ Torr. The process chamber is composed of water-cooled stainless steel with a quartz window through which the infrared tubular halogen lamp furnace can heat the sample. Sample temperature can be monitored by both a contact thermocouple and/or an optical pyrometer below the graphite susceptor that the sample sits on. Annealing processes can be performed in regular ambient conditions, under vacuum, or with an alternate available gas.

An initial concern with the use of the *AnnealSys* RTA was the potential for cross contamination with other materials being annealed. In any thermal reaction process there is the possibility of cross contamination due to material adsorbing on the quartz window from one sample and potentially contaminating later samples. In order to prevent this, a separate dish and cover slip were implemented. For all anneals, the sample was placed inside a quartz dish and positioned underneath a quartz slide. In this way, any released material from the sample would be collected on the underside of the plate, and any potential contaminant from the quartz window itself would be stopped by the top of the quartz slide. Between all anneals, both the slide, and dish were cleaned with water and ethanol before being dried with nitrogen, as well as the annealing chamber being wiped down with ethanol. While this setup highly reduces the probability of any cross sample contamination, there were circumstances in which the vacuum pump utilized was strong...
enough to occasionally relocate a portion of the sample out from underneath the covering slide. To counteract this, a second slide was eventually put into use, and positioned parallel to the cover slide, but lying flat on the bottom of the dish. This small ridge provided enough of a barrier to prevent any sample pieces from moving out from under the cover slide. To accommodate this aforementioned dish and slide apparatus, additional changes to the previous orientation of the chamber needed to be made. From the floor of the annealing chamber to the quartz window there is only 22.5 mm of space available. The height of the plate and dish holder is a static 16 mm that cannot be changed (15 mm for the dish, 1 mm for the slide cover). As built by the manufacturer, the previous combined pin and susceptor height was 7.5 mm (5.5 mm for the quartz pins, and 2 mm for a susceptor height). Without any adaptations to the system, there would be a total height of 23.5 mm. Therefore, two options were explored: the first being to simply remove the susceptor and place the quartz dish directly on the supporting pins, and the second to have glass work performed on a portion of the system to reduce its vertical height. The first option proved unsuccessful due to the fact that quartz, and more generally glasses in general have a very low level of absorption of the optical radiation emitted from the halogen bulbs. Thus, in order to properly optically measure the temperature of the dish, special spectral filters and pyrometers are required. As such, the pyrometer is unable to distinguish between the susceptor radiation and the radiation coming directly from the halogen heating bulbs. By performing a thermocouple controlled trial, in which the temperature was brought up to 600°C, this characteristic was demonstrated, as the pyrometer readout mimicked the power curve of the halogen bulbs rather than the temperature being reported by the thermocouple. Therefore, the only
option was to change one of the dimensions of our system. After consultation with the Glass Blowing Shop within the Department of Chemistry at University of Toronto, it was concluded that the only feasible option would be to cut smaller support pins. The finished chamber apparatus is displayed in Figure 3-2, wherein, the new pins measuring 3.5 mm above the chamber floor were implemented.

![Figure 3-2: Finished sample holding apparatus.]

A second concern was the calibration of the pyrometer for the setup used. Any change in the sample type and setup (i.e. atmosphere, substrate or vertical displacement) can skew the pyrometer readings for similar temperatures. Considering that there was an addition of the quartz dish and a significant lowering of the susceptor much closer to the chamber floor where the pyrometer is physically located, a recalibration was required. In order to calibrate the pyrometer, a temporary, thermocouple was utilized. A thermocouple was inserted into the chamber using an alternate measuring port. A number of processes were run using thermocouple control up to a maximum temperature of 900°C. By comparing the raw binary reading of the pyrometer, to the “actual” sample temperature as determined by the contact thermocouple, a calibration table was created for the aforementioned apparatus. The recipes to be used for sample annealing were
compared using both thermocouple and pyrometer control and process curves were nominally the same.

3.2- **Additional Nanoparticle Characterization Techniques**

In addition to Raman spectroscopy, other methods of characterization of the NPs will be required. This is done primarily to analyze certain characteristics of the NPs that Raman cannot analyze, but also to corroborate the results from Raman spectroscopy that has not been widely investigated to date on colloidal NP systems. While, Chapter 1 touched briefly on the concepts involved with some additional methods of characterization, the additional methods of characterization used in this thesis will be covered with additional detail.

3.2.1- Photoluminescence Spectroscopy (PL)

PL spectroscopy is a standard, optical method of analysis used to characterize the possible optical energy transitions in a semiconductor. In comparison to bulk semiconductors, the quantum size effects of NPs cause the energy bands inherent to semiconductors to discretized and are in fact adjustable depending on the size of the particles. The concept of PL spectroscopy is the same. Figure 3-3 displays a schematic of a radiative bandgap transition that can be probed by PL spectroscopy. When UV light illuminates the material, some of the light is absorbed as long as the excitation light is of greater energy than the bandgap of the material. This absorption creates an electron-hole pair of equivalent energy with the hole (white circle) in the valence band and the electron (black circle) in the conduction band (shown as process I). Subsequently, both the electron and hole relax non-radiatively (often through phonon scattering) down to the
band edge until they reach the lowest available energy level (shown as process II). Finally, the electron and hole recombine across the bandgap and emit radiation proportional to the energy gap in the material (shown as process III). It is this emitted radiation that PL spectroscopy detects offering a means of studying the radiative transitions in the sample material.

![Figure 3-3: Schematic of radiative bandgap transition probed by photoluminescence spectroscopy.](image)

With NPs, this also offers insight into the size and size distribution of the NPs in the sample.

### 3.2.2 Ultraviolet-Visible Spectroscopy (UV-vis)

UV-vis spectroscopy is sometimes used as a complement to PL spectroscopy. In order for PL spectroscopy to be performed, the material must be able to absorb the UV light used to excite the band edge transitions. UV-vis is a study that analyzes the effectiveness of a material to absorb incident light of varying wavelengths. Referring back to Figure 3-3, UV-vis is concerned only with the transition labeled I. A variable monochromatic light is passed through a sample and the remainder is captured after
interaction. By varying the wavelength of the excitation light, the effectiveness of the material to absorb light ranging across the UV and visible spectra can be measured. Figure 3-4 displays a sample absorbance and photoluminescence spectra of CdSe nanocrystals as measured by Murray et al.\textsuperscript{48}

![Example spectra taken from Murray et al.\textsuperscript{48} of both UV-vis absorption spectroscopy (shown on the left axis) and also PL spectroscopy (shown on the right axis).](image)

The wavelength position of both the fluorescence and absorbance spectra are dependent on size, and the sharpness of the peaks of both the luminescent emission and the excitonic peak (closest peak to the luminescent output due to the creation of an exciton within the NP structure) is dependent on the size dispersion of the NPs.
3.2.3- X-Ray Diffraction (XRD)

XRD is of extreme interest in material characterization because it offers insight as
to the crystalline order of the material. The wavelength of X-rays is of comparable length
to the atomic distances in a crystal and as such are suitable for probing the crystalline
structure of a materials. XRD is only applicable to materials that exhibit long range order
or periodicity in their atomic arrangement and is therefore unsuitable for amorphous
materials. However, in crystalline substances, the incident X-rays on the sample as
shown in Figure 3-5 can be reflected from the regularly ordered crystalline planes. The
reflected waves will become interfere with each other, and will be intensified if the
difference in their optical path is a multiple of the incident wavelength according to
Bragg’s Law:

\[ 2d \sin \Theta = n \lambda \]  

(3.1)

where d is the interatomic spacing, \( \Theta \) is the reflected angle, n is the order of the
reflection, and \( \lambda \) is the wavelength of incident radiation. From the collection of the
diffraction pattern from a material, an analysis of crystal structure, crystal size, internal
stresses, and composition can be made.

![Figure 3-5: Reflected X-ray waves from a crystalline structure.](image)
Power XRD when applied to NPs can display slightly different characteristics when compared to the comparable bulk material. In particular, a phenomenon of finite size broadening occurs whereby in crystals of sizes below 100 nm, the diffraction lines broaden with decreasing crystallite size. This is due to the fact that the width of a diffraction peak is inversely dependent on the number of reflections from crystal planes – in other words the thickness of the crystal. Figure 3-6 displays experimental XRD data from Murray et al. and highlights the broadening of CdSe diffraction lines as the size of the nanocrystals change.

![XRD spectra](image)

**Figure 3-6:** Sample experimental CdSe XRD spectra taken from Murray et al. showing the effects of finite size broadening. The different diameters of the nanocrystallites in angstrom are: (a) 12, (b) 18, (c) 20, (d) 37, (e) 42, (f) 83, (g) 115, and (h) displays the bulk wurzite peak positions.

### 3.2.4- X-Ray Photoelectron Spectroscopy (XPS)

XPS is based on the physical process of photoionization. Photoionization is caused by the ejection of one or more molecules from an atom, ion or molecule as a result
of incident X-ray radiation. This process is modeled in Figure 3-7. While, inherently a destructive process, the ejected electron carries information about its preionized state. By capturing and analyzing the kinetic energies of the ejected electrons, the bonding energy can be determined of the bonds present in the material sample. Careful analysis of the kinetic energies of the emitted electrons can provide information on the elemental composition of the material and electronic states of the elements present.

![Figure 3-7: Photoionization of an electron from an atom due to incident x-ray radiation](image)

XPS in NPs can be used to study the organic capping material of the NPs, and also the interaction of the capping layer with the inorganic core. Lobo et al., have used XPS to both identify the presence of atomic species and also to more carefully analyze the bonding energies of the atoms in the system. This in turn can offer insight into the ligand passivation on the semiconductor surface or oxidation of the inorganic core itself.
3.2.5- Transmission Electron Microscopy (TEM)

TEM is a method of imaging a material. Objects smaller than 100nm can be imaged using TEM due to the smaller wavelength of the electrons being used in detection in comparison to that of light used with an optical microscope. TEM operates in a very similar way to that of an optical microscope whereby an electron beam instead of visible light is focused using special lenses onto a sample and then the electrons passing through the sample are projected onto a phosphor screen and enlarged giving an image of the sample. An example of a TEM image from literature is shown in Figure 3-8, where CdSe NPs on the order of 3-4 nm can be identified albeit with a loss of contrast at the NP surface.

![TEM Image](image.png)

Figure 3-8: Sample TEM image from Murray et al., displaying CdSe NPs on the order of 3-4 nm.
Chapter 4. Rapid Thermal Annealing of Colloid CdTe Nanoparticles

A large portion of this thesis is centered on the application of RTA to colloid semiconductor QDs. As has previously been identified in the preceding chapters, CdTe NPs are of extreme interest in areas including inexpensive efficient solar cells, ultrafast electron transfer, biological imaging or labeling and negative refractive index materials.\(^{12}\)\(^{17}\) For use in optoelectronic devices, a highly crystalline semiconductor core is particularly desirable, however, such properties are difficult to influence exclusively through the particle growth process. As such, post synthesis adaptation of QDs is an area of extreme value.

4.1- Material Selection

Two options for QD material were available from the Toronto based company Vive Nano. Both were CdTe QDs that were capped by PAA, and the only difference between the two was the size of the particles and subsequent fluorescent output of the dots. One had a PL centered at 525 nm and was classified as “green” CdTe, the second had a PL centered at approximately 660 nm and was classified as “orange” CdTe. Initial Raman measurements using Teflon capillary tubes (TCT) were performed to determine the suitability of each material to Raman analysis. Shown in Figure 4-1 and Figure 4-2 are the Raman spectra of the orange and green CdTe NPs respectively. As can be seen, there is a significant fluorescence occurring in the orange sample. This fluorescence is overlapping the wavenumber region of particular interest between 100 and 300 cm\(^{-1}\),
where all of the CdTe Raman active modes are located. This fluorescence is not present in the scan of the green sample.

Figure 4-1: Raman scan of orange CdTe NPs using TCT

Figure 4-2: Raman scan of green CdTe NPs using TCT
This fluorescence is a result of the orange NPs having their bandgap excited by the analysis laser used in the Raman scans. The laser being used is a HeNe laser that emits at 633 nm. As such, the laser has adequate energy to excite the orange NPs while not enough to excite the green NPs. In order to avoid this inherent fluorescent interference a laser wavelength below the output fluorescence of the orange NPs would have needed to be used. However, as only 633 nm and 532 nm laser lines were readily available at the University of Toronto, the only option was to focus the annealing study solely on the green CdTe NPs.

4.2 - Experimental Procedure

Dried PAA functionalized CdTe NPs were obtained from Vive Nano Inc. The RTA process recipe was designed as follows:

Step 1: Reduce chamber pressure over 30s to a minimum of ~100Pa.

Step 2: Introduce Argon into the chamber over 120s to reach a maximum of 100kPA (room pressure).

Step 3: Set the heating coils to 8% power for 7s to heat the system to the pyrometer threshold of 100°C.

Step 4: Heat the sample at 50°C/s to the desired annealing temperature – the amount of time in this step is dependent on the final temperature.

Step 5: Maintain chamber temperature at set point for 30s.

Step 6: Cut coil power and allow chamber to cool for 300s.
Step 7: Reduce chamber pressure over 30s to a minimum of ~100Pa.

Step 8: Introduce Argon into the chamber over 120s to reach a maximum of 100kPa (room pressure).

In Steps 1 and 2, the room atmosphere is removed and replaced with Argon for two reasons. Primarily, to remove any atmospheric contaminants such as dust particles that may potentially be baked onto the sample. Secondly, Argon is an inert gas and at room temperature it is non-toxic and creates no known stable compounds, as such, its use in annealing can help prevent any carbonizing of the sample that would ordinarily occur under a standard oxygenated atmosphere.

Due to the limitations of the pyrometer used for temperature sensing, Step 3 was required to initially bring the temperature of the system up to a readable level. The pyrometer is unable to discern differences in temperatures below 100˚C. To prevent potentially dangerous heating or machine operation due to incorrect temperature readout, the power of the heating coils is actively controlled to bring the chamber temperature up to approximately 100˚C, thus resulting in a “correct” temperature value of the system.

A constant temperature gradient of 50˚C/s was used in the annealing of the QDs, so the rapid heating step varied in length depending on the end temperature, from 2 seconds for a 200˚C anneal to 12 seconds for a 700˚C anneal. One additional control sample was created by subjecting the as-grown NPs to Argon and vacuum processing steps with no heat applied, however, it displayed no differences of results from the Raman and PL spectra and as such, the other tests such as UV-vis, XRD, XPS, and TEM were not performed. After the 30s heating step, the chamber cools simply through the
conduction of heat from the chamber via cooling water. The chamber is not actively cooled however, only through the heat transfer between the chamber and the circulating water is the temperature reduced. In highly sensitive anneals, this could lead to discrepancies in the anneal times at different temperatures since it will take longer for a hotter chamber temperature to cool down to a level that no longer influences the sample.

Following cooling, the chamber atmosphere is again removed and replaced with Argon to remove any potentially harmful toxins that may have been released into the atmosphere during the annealing process.

Initially, the annealing process was applied on six samples of CdTe and the processing temperature ranged from 110°C (minimum RTA temperature obtainable was 110°C rather than 100°C) to 700°C with a 100°C differential between samples. An unannealed control was maintained. Throughout the annealing process, data was gathered on the theoretical set point temperature, the actual pyrometer readout, and the power being applied to the heating coils. Figure 4-3 displays the annealing process for the 400°C annealed sample. The characteristics of the annealing process are nominally constant across all temperatures. As can be identified in Figure 4-3, there are two slight issues with the heating curves. The first is that there is an inherent delay in the temperature readout of the pyrometer causing the heating curve to trail the idealized temperature curve. This is an unavoidable side effect of using a highly accelerated heating gradient due the finite time it requires for the carbon sample plate to heat up and then emit radiation for the pyrometer to collect. The second issue is the overshoot of the maximum set temperature for the annealing process. Again, this is a result of the high ramping temperature and the time required for the pyrometer to catch up to the actual
chamber temperature. Through slight adjustments of the feedback properties of the control system, this overshoot has been limited to 5-10°C and is acceptable for this procedure.

![Figure 4-3: Example of a 400°C rapid thermal annealing temperature and power output curve](image)

4.3- Initial Processing Observations

Following the procedure outlined in 4.2-, samples were processed from 200°C to 700°C. Initially, using the raw material directly from Vive Nano, results were mixed on the repeatability of the annealing process. The significant problem was that different runs of the same temperature on the same batch of sample would result in varying levels of burning. It was difficult to determine prior to annealing whether the sample would be carbonized after the process resulting in a non-soluble destroyed material or if the sample
would remain intact. While there was never any carbonization observed for samples annealed at below 300°C, from 400°C and higher, the sample would at times be burnt and other times not. Shown in Figure 4-4 is an example of one of the samples that burnt after undergoing a 500°C annealing process. As can be seen, a portion of the larger piece of the sample is blackened along with several other flakes. Following redispersion in water, it is shown in Figure 4-5 that while the uncarbonized material still was able to dissolve in water, the burnt portion was not and remained as visible flecks within the solution. While measurements could still be performed on the solution, it was impossible to completely separate the burnt material from the soluble portion. As such, any measurements are inherently skewed due to an imbalance in sample concentration. Through a number of trial and error runs, it was determined that both the larger and closely packed flakes of material had a higher susceptibility to burning. By choosing the relatively small flakes of NPs and spreading them out as much as possible underneath the cover slide, the chance of burning the material was greatly reduced. Using this technique, the burning of samples at or below 600°C was virtually abolished. Occasionally burning still occurs but at a small enough frequency that it is not a current significant concern. It is also not known exactly why the larger pieces of material burn as opposed to the separated smaller flakes, but this phenomenon was not investigated.
Figure 4-4: Example of a sample burnt after 500°C annealing

Figure 4-5: Example of a sample burnt after 500°C annealing upon redispersion in water

Although the process at or below 600°C was corrected to minimize the chance of carbonization, this was not the case annealing at 700°C. The 700°C annealing process would burn regardless of sample size and spread. After all runs, most if not all of the sample was carbonized and blackened as shown in Figure 4-6 and the cover slip above the sample showed residue from burning polymer.
It was determined that the recoverable sample would not disperse well in water as demonstrated in Figure 4-7 due to the fact that the soluble polymer capping could not withstand the 700°C annealing temperature and was destroyed. Due to this fact, the 700°C process was deemed unsuitable for our material and further analysis on the sample was not performed.

Figure 4-7: Example of a sample burnt after 700°C annealing upon redispersion in water.
As a pictorial example of a properly annealed sample with no burnt portions and smaller flakes is shown in Figure 4-8. As can be seen in Figure 4-9, the annealed material dissolved completely in water with no visible burnt flakes.

Figure 4-8: Example of a sample annealed properly at 600°C

Figure 4-9: Example of a sample annealed properly at 600°C and dispersed in water.

4.4- Material Analysis

Following the annealing, the samples were studied using six different analysis methods. The three optical methods used were UV-visible absorption spectroscopy (UV-vis), photoluminescence (PL) spectroscopy and Raman spectroscopy. For the optical
analysis, the solid samples including a control were reweighed and dispersed in water to obtain a 2mg/mL concentration in all cases. The non-optical methods were x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), and transmission electron microscopy (TEM).

4.4.1- Photoluminescence Spectroscopy

50uL aliquots were taken from the remaining samples and the fluorescence spectrum of the QDs were obtained using a room temperature Tecan Safire system. The samples were excited by UV light of 375 nm and the emission spectrum was gathered between 400 nm and 850 nm. Figure 4-10 shows the obtained curves from the six samples tested.

![Photoluminescence spectra from the unannealed and annealed samples.](image)

Figure 4-10: Photoluminescence spectra from the unannealed and annealed samples.
Using these spectra, a peak fitting routine contained with the Labspec 5 software was applied to obtain Gaussian-Lorentzian approximations of the PL peaks. Table 1 tabulates the critical peak values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak</th>
<th>Amp</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed</td>
<td>528.91</td>
<td>9645.08</td>
<td>62.7759</td>
</tr>
<tr>
<td>200C</td>
<td>528.176</td>
<td>9922.5</td>
<td>61.8025</td>
</tr>
<tr>
<td>300C</td>
<td>528.166</td>
<td>9664.27</td>
<td>60.5776</td>
</tr>
<tr>
<td>400C</td>
<td>528.172</td>
<td>8870.67</td>
<td>60.6661</td>
</tr>
<tr>
<td>500C</td>
<td>530.489</td>
<td>6128.84</td>
<td>62.5891</td>
</tr>
</tbody>
</table>

It can be seen that the annealing does not affect the fluorescent intensities of the NPs for annealing at 200°C and 300°C. The minute intensity variations between the two lowest temperature anneals and the control sample could easily be caused by small inaccuracies in sample weight, concentration, and volume. Progressing to higher temperatures there is a slight intensity reduction of approximately 8% in the 400°C annealed sample, where again sample handling could play a factor in the reduction but the intensity is still very close to the unannealed sample. However, the 500°C and 600°C samples display a much larger intensity loss than the other anneals with only 64% and 47% of the unannealed fluorescence respectively. While this reduction is somewhat detrimental from a device point of view, it should be noted that the intensity only drops by a factor of two at 600°C, which is comparable to results obtained through conventional annealing at temperatures of only 180°C.\textsuperscript{22} The intensity reduction is attributed to a change in the density of trapped states on the surface of the NPs. Trapped surface states and changes in the capping layer of the NPs have a high impact on the fluorescence.
output of luminescent quantum dots. The other significant statistic is that for the samples annealed from 200°C to 500°C, there was no change within error of the peak wavelength position and the FWHM bandwidth and there is only a slight increase of both in the 600°C annealed sample. Since the emission wavelength of the quantum dot fluorescence is directly dependent on the size of the quantum dot, it can be concluded that the annealing process does not adversely change the NP size.

4.4.2- UV-visible Absorption Spectroscopy

Absorption spectra were obtained from the aqueous solutions using an Agilent 8453 UV-visible spectrometer. Figure 4-3 shows the UV-vis absorption results of both the un-annealed and 600°C annealed sample. UV-vis absorption results resulted in no changes between the as-grown sample and any of the sample annealed below 600°C. These UV-vis results simply reinforce the fact that annealing is not changing the size of the nanoparticles. From Figure 4-11, there is no change in the absorption of the samples annealed up to 500°C, and as can be seen, only a very slight red shift in absorption in the 600°C annealed sample, which corresponds with the slight shift in the fluorescence of the same sample.
4.4.3- Transmission Electron Microscopy

Further insight into the structure of these polymer stabilized NPs was obtained from the TEM pictures. TEM was performed on a conventional Hitachi H-7000 electron microscopy operating at 100 KV and 30 mA beam current. Samples for TEM were prepared by putting a few drops of a solution containing CdTe NPs on an amorphous carbon substrate supported on copper grid and allowing the solvent to evaporate at room temperatures. Figure 4-12 displays a comparison between the as grown and 500°C annealed NPs. From the TEM images, it can be seen that the NPs have an approximate diameter of 3-5 nm. Also, TEM image of the sample annealed at 500°C does not display any obvious changes in particle size or any NP agglomeration. These findings are similar
regardless of annealing temperature and the images show no change in particle size with annealing. The TEM analysis further supports the previous UV-vis and PL data that the annealing of the NPs leaves size of the particles nominally unchanged.

Figure 4-12: a) TEM picture of the as-grown NPs. b) TEM picture of the NPs after annealing at 500°C.

4.4.4- Raman Spectroscopy using HC-PCF

The Raman properties of the NPs were studied through the use of HC-PCF obtained from Crystal Fibre Inc. to co-propagate the laser source in the liquid sample. The sample and fiber preparation steps followed were identical to the procedure outlined by Irizar et al., whereby a 6.5cm length of HC-PCF was stripped and cleaved, prior to collapse of the cladding holey structure at one end of the fiber using a fusion arc splicer that left the central core of the HC-PCF open. Then, by inserting the fused end of the fiber into a small well of the sample to be investigated, capillary action acts to selectively fill the central core of the fiber. The fiber used and pictured in Figure 4-13 is the HC-800, and is designed specifically to propagate light along the central core of the
waveguide with a wavelength of approximately 800 nm. Unfortunately, fibers that guide light at wavelengths of around 633 nm were unavailable from Crystal Fibre Inc.

![Cross sectional image of the HC-800 fiber from Crystal Fibre Inc.](image)

**Figure 4-13:** Cross sectional image of the HC-800 fiber from Crystal Fibre Inc.

Thus, while the photonic band gap effect that guides light in properly designed PCF may play some role in the guiding of light through the fiber, the main portion of the light is guided by total internal reflection (TIR). TIR is possible since the cladding structure is composed of mostly air holes with a skeleton of silica maintaining structural stability. An effective refractive index of the cladding structure has been previously modeled and is found to be approximately 1.262 at a wavelength of 633 nm. The criteria for TIR to occur is that the refractive index of the core be higher than the refractive index of the cladding structure surrounding it, thus, when investigating aqueous based solutions with refractive indexes around 1.33, this restriction is satisfied. Raman scans were performed using the previously outlined *Horiba Jobin Yvon H800* integrated Raman system. The resulting spectra are displayed in Figure 4-14.
Figure 4-14: Raman spectra of annealed and as-grown NPs.

From these spectra, three Raman active peaks in the dispersed solution were assigned. The three assigned peaks correspond to the Te A1 mode at ~127 cm\(^{-1}\), the Te E mode at ~141 cm\(^{-1}\), and the CdTe LO mode at ~165 cm\(^{-1}\).\(^{52-54}\) Due to the modes’ finite width and overlapping frequencies, there could also be a portion of the Te E peak contributed to by the CdTe phonon mode that is located at ~140 cm\(^{-1}\). The presence of the two Te peaks have previously been attributed to both Te inclusions within a CdTe crystal and also defects along the boundaries of the material.\(^ {53,55}\) Unfortunately, from the Raman measurements it is not feasible to quantify the amount of Te inclusions or defect bonds due to the fact that Te bonds exhibit a relatively high Raman cross section and subsequent scattering signal in comparison to CdTe. What is apparent simply from the Raman spectra is that the contribution of the Te defect modes decreases significantly with
increased annealing temperature. After taking Raman spectra of just a water filled HC-PCF, it was determined that the background contribution from the fibre and solvent (water), contributed three broad peaks located at 150 cm$^{-1}$, 178 cm$^{-1}$, and 225 cm$^{-1}$. Removing these from the NP spectra allowed Gaussian-Lorentzian peaks to be fitted to the aforementioned Cd-Te and Te-Te modes. Due to changes in the intensity of the spectral background between samples, direct amplitude comparison between peaks was not feasible. The different background intensities could be attributed to a number of sources such as small differences in NP concentration, defects in the PCF, or the presence of air bubbles within the PCF itself. The cause of such perturbations was not directly investigated but rather, a comparative study of different peaks within the same sample was devised to negate the effects of the non-constant background. Further investigations and discussion relating to absolute Raman intensity is covered in Chapter 5. By comparing the amplitude of the CdTe LO mode to that of both the Te A1 and Te E modes of the same sample, the effects of a changing background can be eliminated since the background will have the same impact on both of the peaks. Figure 4-15 displays the amplitude ratios of both the Te A1 and Te E modes as compared to the amplitude of the CdTe LO mode.
The ratio values are obtained simply through the formula:

\[ \text{Amplitude Ratio} = \frac{\text{Amp}_{\text{Te}}}{\text{Amp}_{\text{CdTe}}} \]  \hspace{1cm} (4.1)

By using this formula and comparing the different sample ratios to each, the comparative detection of a more or less crystalline core can be made. The smaller the amplitude ratio, the less impact the Te defect modes have on the spectra in comparison to the CdTe LO mode. As such, a smaller ratio correlates to less Te defect bonds within the crystal and subsequently a more crystalline semiconductor core. Looking at the values in Figure 4-15, it is obvious that with increased annealing temperature there is a reduction in the intensity of the Te phonon peaks in relation to the CdTe mode. While the as-grown, 110°C and 200°C samples display nominally the same ratio, annealing above 200°C results in a decrease of both the compared ratios. Looking at the Te A1 to CdTe LO
ratio, the value of 19.52 after 200°C annealing decreases to a minimum of 2.20 in the 600°C annealed sample. Similarly, the ratio of Te E to CdTe LO drops from a maximum of 10.47 at 200°C annealing to 0.65 with 600°C annealing. It can thus be concluded that the RTA process above 200°C results in the removal of Te defects within the semiconductor core. Looking more critically at the results, it is significant to note that most of the ratio change occurs between the temperatures of 200°C and 400°C with little to no change outside of that temperature range. Both amplitude ratios reduce by approximately 50% in the 300°C annealed sample and almost to a minimum at 400°C. This leads to the inference that annealing is affecting the NP core most drastically between the temperatures of 200°C and 400°C. Increasing the temperature while maintaining constant anneal times, progressively moves the NPs further along in a crystallization process and thus the Raman amplitude ratios displayed in Figure 4-15 are obtained.

4.4.5- X-Ray Diffraction

Since the Raman scans were identifying a small crystalline change within the semiconductor core of the NPs, an additional test to confirm the crystalline change is XRD. All XRD spectra were performed by a Rigaku Ultima III pXRD with Cu Ka source (1.5418 Å) and Si powder was used as an internal standard. The XRD measurements required between 30 mg and 50 mg of sample, which is significantly more than the 5-6 mg required for all of the previous measurements combined. As was addressed earlier, annealing of larger amounts of NPs at higher temperatures caused carbonization so XRD spectra on the 500°C and 600°C annealed samples were unobtainable. Regardless, samples corresponding to the region with the most change as identified by the Raman
results (between 200°C and 400°C) were successful. Shown in Figure 4-16 are the XRD spectra from the unannealed, 200°C, 300°C, and 400°C NP samples. Overlay in the graph are the markers corresponding to powder diffraction lines from zincblende type CdTe (solid circle, solid lines) and wurzite type CdTe (open square, dotted line). In the unannealed spectrum, there are three peaks that indicate the presence of zincblende CdTe at 24°, 40°, and 46°. These correlate to reflections from the zincblende 111, 220, and 311 planes respectively. In addition, there is a feature creating a shoulder off of the zincblende 111 peak at approximately 29°. While this feature is not clearly defined it can be attributed to either irregularities and randomizations present in the crystal or it could correlate to the 102 plane found in wurzite CdTe. Without exploring further into the cause of the shoulder at 29°, what is evident from the annealed spectra is that this feature systematically decreases with annealing temperatures of 300°C and 400°C. While there is a slight and insignificant increase of the FWHM of the zincblende 111 crystalline peak in the 300°C annealed sample, the feature at 29° has already been reduced inferring a transition to the zincblende structure. At 400°C, the extraneous feature is depleted almost completely and the XRD spectrum clearly displays a CdTe crystal of zincblende structure. These results suggest that the annealing of these NPs causes the semiconductor core to align to purely zincblende structure if an adequately high process temperature is utilized. This prevalence of the zincblende crystalline phase corroborates previously documented research CdTe QD annealing. This crystalline reorganization occurs over the same temperature range for which the largest decrease in Raman mode ratios was observed. As the exact cause of the shoulder at 29° cannot be verified using the techniques employed, both explanations are explored. If in the first reasoning, it is
assumed that the feature at 29° is a result of the 102 plane in wurzite CdTe, it can be inferred that the RTA process above 200°C acts to convert the presence of any wurzite CdTe to the zincblende type. With the conversion of the wurzite type crystal to zincblende creating a nearly homogeneous crystal, there will be less grain boundaries between different phases and as such a decrease in defect Te bonds. This would account for both the trends seen in the XRD spectra and also the Raman scans. On the other hand, if the feature at 29° is attributed to randomization in the crystal due to the growth mechanisms, the RTA process then serves to remove these crystal defects. Fewer defects would again correspond to a reduction in defect Te bonds, corroborating the Raman mode ratios observed previously. Regardless of specifically what is causing the non-zincblende feature in the CdTe, what is significant is that with increased annealing temperature the purity of the zincblende crystal phase is enhanced. What is most exciting is that this crystalline enhancement is demonstrated without adversely affecting the PL of the particles as is seen with conventional annealing.22 The need for an annealing option that does not negatively affect the PL efficiency has been voiced by Niu et al..22 While this is only an investigation of the effects of RTA on the QD material itself and not a device, certain phenomena of this experiment may carry over, but will need to be tested explicitly on a device to be certain.
Figure 4-16: XRD of as-grown and annealed NP samples up to 400°C. Powder diffraction lines of wurzite (□) and zincblende (●) type crystalline CdTe markers are shown as references.

4.4.6- X-Ray Photoelectron Spectroscopy

The final technique used to evaluate the effect of annealing on the CdTe NPs was XPS. A *Thermo Scientific Theta Probe XPS* spectrometer (ThermoFisher, E. Grinstead, UK) was used for XPS analysis. A monochromatic Al Kα X-ray source was used, with a spot area 300 μm. Charge compensation was provided utilising the combined e+/Ar+ flood gun. Position of the energy scale was adjusted to place the main C 1s feature (C-C) at 285.0 eV. Peak areas were obtained from spectra run in low resolution mode (pass energy = 200 eV). Elements of interest (C, Cd, and O) were also run in high resolution mode (30 eV pass energy). This was not done for Te since the signal was extremely
weak. However, the Te 3d peak was also fitted as the separation of the oxide was easily resolvable from the CdTe itself. Instrument control and all data processing was performed using the software (Avantage) provided with the instrument. Displayed in Table 2 and Table 3 are the elemental analyses for the as grown and 300°C annealed NPs respectively. The values in Table 3 are representative of all other annealing temperatures. The only noticeable difference with annealing was the near complete disappearance of the Cl2p in the sample. The processing of the NPs involves a precipitation of the particles with a NaCl solution. As expected in the as grown sample, both Na and Cl are present in the XPS spectra. However, in all subsequent XPS analysis on annealed samples, although the Na was still present, the Cl has disappeared. While this phenomenon is interesting to note, neither the Na nor the Cl play an active role in the finished structure or properties of the NPs and as such was not further investigated.

Table 2: Elemental analysis for as grown NPs.

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak BE</th>
<th>FWHM eV</th>
<th>Area (P) CPS.eV</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>285.00</td>
<td>1.60</td>
<td>27375.52</td>
<td>64.80</td>
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<tr>
<td>Cd3d5</td>
<td>405.61</td>
<td>1.61</td>
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<tr>
<td>Cl2p</td>
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</tr>
<tr>
<td>Na1s</td>
<td>1072.19</td>
<td>1.82</td>
<td>23883.17</td>
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<tr>
<td>O1s</td>
<td>531.58</td>
<td>1.80</td>
<td>16784.56</td>
<td>14.70</td>
</tr>
<tr>
<td>Te3d</td>
<td>572.82</td>
<td>1.61</td>
<td>2612.50</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 3: Elemental analysis for 300°C annealed NPs.

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak BE</th>
<th>FWHM eV</th>
<th>Area (P) CPS.eV</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>284.93</td>
<td>1.52</td>
<td>40451.39</td>
<td>73.18</td>
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<tr>
<td>Cd3d5</td>
<td>405.49</td>
<td>1.62</td>
<td>10336.35</td>
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</tr>
<tr>
<td>Cl2p</td>
<td>198.47</td>
<td>0.96</td>
<td>696.85</td>
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<tr>
<td>Na1s</td>
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<tr>
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<tr>
<td>Te3d</td>
<td>572.56</td>
<td>1.72</td>
<td>2719.56</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Identified in Figure 4-17 is a comparison between the as grown and 300°C annealed sample for the C, Cd, and Te regions of interest. In (a) and (d) of Figure 4-17, the core level C1s spectra is deconvolved into three components with binding energies at 285.43 eV, 286.36 eV, and 288.37 eV corresponding to carbons in different chemical formations (C-C, (C)-C=O and (O)-C=O, respectively. These peak components are specifically assigned to the PAA chains and demonstrate the incorporation of the organic polymer layer around the NP surface.\textsuperscript{56} No trends or changes in the carbon peaks could be identified with annealing of the NPs, thus indicating that the polymer capping is nominally unchanged by the processing. Depicted in Figure 4-17 (b) and (e), are the Te peaks of the XPS scan. The peak at 572.63 eV is attributed to Te 3d\textsubscript{5/2} in the form of CdTe and that of 575.95 to Te 3d\textsubscript{3/2} in TeO\textsubscript{2}.\textsuperscript{56} The XPS shows trace amounts of Te oxides, however, its content cannot be seen from the elemental analysis and there was nominally no change in the level of TeO\textsubscript{2} in comparison to CdTe. Shown in (c) and (f) of Figure 4-17, the presence of the Cd 3d\textsubscript{5/2} peak at 405.56 eV and Cd 3d\textsubscript{3/2} at 412.20, clearly indicate that Cd exist in the form of CdTe.\textsuperscript{56} Again, there is no change in the shape or position of the maxima of the deconvolved peaks due to thermal annealing, suggesting that Cd and Te are still bound together at all times.
Figure 4-17: a) High resolution XPS of C 1s scan of (a) as grown samples, (d) 300°C annealed sample: the peak labelled 1 is the C-C bond, the peak labelled 2 is the (C)-C=O bond and the peak labelled 3 is the (O)-C=O bond. 3d Te scans (b) as grown samples, (e) 300°C annealed and 3d Cd scans (c) as grown samples, (f) 300°C annealed sample.

Not pictured is a comparison between high resolution O1s level, high resolution spectra that demonstrates two peaks at 532.41 and 533.81 eV. The intensity of the peak at higher binding energy (533.81 eV) is attributed to the unbound (OH) groups of the organic polymer layer. Shown in Table 4 is the value of the fitted peak to the unbound (OH) group at 533.81 eV. As can be seen, the atomic percentage of oxygen in this form decreases with annealing above 200°C. This is an expected result as is due to excess water present even in the dried NP evaporating with increased annealing temperature. As there is nominally no change in the oxide versions of the Cd and Te, it can be concluded
that the aforementioned oxygen trend with annealing is not interfering with the CdTe semiconductor core and is contained solely within the polymer itself.

### Table 4: Fitting for the O1s peak at approximately 533.81 eV and contribution to spectra values

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Peak BE</th>
<th>FWHM (eV)</th>
<th>Area (P)</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>As grown</td>
<td>533.79</td>
<td>1.06</td>
<td>100.72</td>
<td>7.01</td>
</tr>
<tr>
<td>200</td>
<td>533.66</td>
<td>1.06</td>
<td>104.94</td>
<td>8.57</td>
</tr>
<tr>
<td>300</td>
<td>533.66</td>
<td>1.06</td>
<td>70.27</td>
<td>3.05</td>
</tr>
<tr>
<td>400</td>
<td>533.96</td>
<td>1.06</td>
<td>29.6</td>
<td>1.76</td>
</tr>
<tr>
<td>500</td>
<td>533.83</td>
<td>1.06</td>
<td>42.4</td>
<td>2.72</td>
</tr>
<tr>
<td>600</td>
<td>533.81</td>
<td>1.06</td>
<td>45.93</td>
<td>1.62</td>
</tr>
</tbody>
</table>

Using the information on the carbon bonding within the material, it can be concluded that there is a polymer capping layer present at all annealing temperatures tested. However, the atomic levels of Cd and Te are too small to see any conclusive changes in the bonding within the semiconductor core itself. In addition, though there is a reduction of unbounded (OH) with higher temperature anneals, the oxygen is bonding with neither the Cd nor the Te in the core, as no change in XPS spectra of either elements is seen. While XPS does not contribute any information to the nanoscale crystalline changes occurring within the core of the NPs, the static nature of the carbon bonding supports the inference that the PAA surrounding the core is nominally unchanged.
Chapter 5. A Setup for In Situ Raman Spectroscopy in Liquid Core Waveguides

The previous chapter has demonstrated the application of HC-PCF as a suitable LCW for the investigation of CdTe NPs. However, the methods and materials utilized in Chapter 4 may pose limitations on Raman sensing in other systems or on other materials. Primarily, the ultimate goal of in situ monitoring of the growth process of colloidal NPs or other reactions is unobtainable without a circulation pump. Having the ability to accurately monitor and investigate the changes occurring in a solution with a close to real time in situ testing system would provide incalculable insight into the colloidal technologies in use today. Using an active pumping system to fill LCWs with sample could expand the characteristics of samples to be studied. For example, the filling time and capabilities of a LCW using capillary action is dependent on sample viscosity, surface tension, and contact angle with the liquid. If an active pumping system is used instead, the exclusivity of sample characteristics for capillary action filling are negated. A separate issue with the PCF that could prove detrimental depending on sample characteristics is the radius of the LCW. Using NPs as an example, if the polymer chains capping the core are large enough or if the NPs tend to aggregate together rather than disperse homogeneously, the particles may not even be able to enter the extremely small radius of the HC-PCF. In this case, a larger core HC-PCF or separate LCW altogether, such as TCT, would need to be used. To implement and study an active filling system, a peristaltic pump was purchased from ThorLabs. Investigations into the capabilities of
being able to clean previously used segments of HC-PCF for reuse, and to actively pump solution into both types of LCW were performed.

5.1- **Pump Characteristics and Operation**

The pump obtained was manufactured by Control Company and has capabilities of a variable flow rate from 0.005 mL/minute to 600 mL/minute depending on user settings and diameter of tubing used. Since the internal diameters of both TCT and HC-PCF are extremely small (110.76 µm and 9.35 µm respectively), the smallest tubing size and thus slowest pumping options were chosen. However, even the smallest pump tubing size had an inner diameter of 508 µm which is nearly five times larger than the TCT and more than fifty times larger than the HC-PCF core. Figure 5-1 is a picture of the peristaltic pump purchased and displays the speed and directional control knob and switches on the left, a rotor in the center with a silicone tube wound around it.

![Figure 5-1: Picture of the peristaltic pump purchased for cleaning and continuous circulation of samples.](image_url)
The entrance and exit tubing can be seen leading out the right hand side of the picture, with the exit terminal on the top and the entrance tube is on the bottom.

The operation principles of this peristaltic pump is simplistic in that the pump operates by running a motor that is attached to the rotor with rollers built onto it. The continuous turning of the rotor causes the rollers to progressively pinch shut the silicone tube and force the fluid within the tube forward by means of positive displacement. It is important to note that there are three rollers on the rotor so that at any given time there is always one pinch point on the tubing preventing any back flow that may occur if the tube length was completely open.

5.2- Liquid Circulation into Liquid Core Waveguides

5.2.1- Hollow Core – Photonic Crystal Fibers

Due to the high cost and preparation time involved in stripping and splicing the PCF, developing the pumping apparatus for circulating sample into the PCF and developing a cleaning procedure would allow for reuse of the fiber lengths and potentially filling of longer PCF strands. To ensure the pumped fluid from the pump would flow through the LCW core, a watertight seal between the silicone pump tubing and the LCW is required. However, because of the mismatch between the 508 µm diameter of the pump tubing and the 220 µm outer diameter of the acrylate coating surrounding the HC-PCF, a connector was required to tightly seal the joint between the two types of fibers. To connect the fiber to the end of the tubing a SMA 905 stainless steel fiber connection manufactured for 230 µm diameter fibers was utilized. While this type of connector is not specifically designed for transfer of liquids, the fiber created a
A watertight seal at the output of the connector and Teflon tape was applied to seal the entrance to connection from the pump itself. Three different types of prepared fibers were used for testing the cleaning procedure: a previously used fiber from the CdTe NP experiments, a newly prepared fiber that has been spliced, and an unspliced fiber. The use of these three different types of fibers ensures that there are no problems with prior contamination, or splicing effects preventing proper fluid flow. At the same time, testing used HC-PCF strands allows for evaluation of the effectiveness of the water circulation in order to develop a proper cleansing procedure. First attempts at circulating the water through the fiber were attempted using the highest speed of the pump to accelerate the cleaning process of the fibers. Unfortunately, while the pump was able to effectively push air through the tubing, SMF connector, and fiber, it could be seen that while water could reach the entrance to the PCF there was no water exiting the end of the fiber. Systematically adjusting the pumping speed down to the lowest setting provided no improvement as liquid was still unable to flow through the test fibers. It was verified that liquid was traveling to the entrance of the PCF by the fact that the instant the fiber was removed from the SMF exit hole, water began to bubble out of the vacancy. Upon further investigations by depositing periodic air bubbles in the water in the tubing, it could be seen that the fluid would move consistently through the fiber until the leading edge of the liquid reached the fiber. As soon as this occurred, the indicator air bubbles could be seen to move a small distance forward, before eventually flowing backwards to its starting position, then repeating this movement. When the liquid reached the fiber, the net displacement of fluid in the tubing became zero. The occurrence of the rapid backflow of the liquid was found to correlate to the point at which one of the rollers
would cease pinching shut the tubing at the top of the rotor. It is postulated that the large mismatch between the tubing diameter and the HC-PCF core is responsible for the lack of fluid flow through the fiber. Even in the best case scenario, with the cladding holes not collapsed, the core and holey region only comprise of a 40 µm diameter. As such, pumping the liquid through the tubing at a constant speed will result in an abrupt throttling of the liquid at the interface between the large and small hole diameters. While this thesis will not venture deeply into the realm of fluid mechanics, in order to maintain fluid flow over a decrease of tube diameter requires the liquid to increase speed so as to conserve mass (volume) flow rate. An elementary calculation when dealing with moving fluids in completely filled circular pipes is:\(^{(5.1)}\)

\[
v = \frac{Q}{A}
\]

where \(v\) is the velocity of the fluid, \(Q\) is the volume rate of flow, and \(A\) is the internal cross sectional area of the pipe. In the peristaltic piping system, the slowest volume flow is 0.005 mL/min, which, when doing the proper calculations results in a fluid velocity of 4.11x10\(^{-4}\) m/s in the silicone tubing, however, using the same mass flow rate, through the HC-PCF (modeled using a 9.5 µm diameter), the fluid velocity required would be 1.18 m/s. This is also the ideal case where the silicone tubing enters the HC-PCF directly without the SMF connector that actually increases the cross sectional area prior to connecting to the fiber. This is a change in velocity of over three orders of magnitude over a very small distance (nearly instantaneous). Then, using Bernoulli’s equation that governs laminar fluid flow in pipes:\(^{(5.2)}\)

\[
\frac{v^2}{2} + \psi + \frac{p}{\rho} = X
\]
where \( X \) for sub-mach speeds and laminar flow is a constant, \( v \) is the velocity of the fluid, \( p \) is the pressure in a pipe, \( \psi \) is gravitational potential, and \( \rho \) is the density of the fluid.

Assuming constant \( \psi \), and that Bernoulli’s equation applies, a change in pressure between the two sections hole diameters will be 700 Pa.

It is speculated that the failure in the case identified above is the finite time that the pump can provide forward pressure before the seal offered by the roller disappears due to continuous turning and backflow occurs. Creating a gradual decrease in hole diameter may improve results of getting the water to enter the fiber, but the logistics of creating a tapered connection between the tube and fiber on the micron scale required is not trivial. Whether or not these theories are correct is irrelevant since the final goal of pumping fluid through the PCF is unobtainable using the current pump, tubing diameters, and fiber diameters available.

5.2.2- Teflon Capillary Tubes

While the pump was unsuitable for circulating water through the PCF, the core of TCT with a 111.76 \( \mu \)m core is more than an order of magnitude larger than that of the PCF. To fit the TCT into the pumping system, no special fitting was required. Due to the naturally elastic nature of the silicone tubing, it was possible for the inner 509 \( \mu \)m hole to be stretched out to encompass the outer 889 \( \mu \)m diameter of the TCT. Once released, the tubing contracted and created an effective seal ensuring that any liquid being pumped would flow through the TCT. Initial circulation tests with the TCT inserted resulted in water being able to be pumped through the TCT core at both minimum and maximum motor speeds. In comparison to the PCF, applying Equations (5.1) and (5.2) to
the new situation, gives values of fluid speed of $8.65 \times 10^{-3}$ m/s and a change in pressure of $3.73 \times 10^{-2}$ Pa. With the peristaltic pump demonstrated effective for circulating liquid through the TCT, further investigations into the length effects of a LCW on Raman signal as derived in Chapter 2, could be pursued.

First, in order to pump various samples into the TCT for proper Raman measurement, a proper cleaning procedure needed to be developed to remove the possibility of cross contamination. In order to properly remove all contaminants, the initial cleaning process created was to first cleanse with water to remove water soluble materials (primary use of this pump), followed by a methanol cycle to remove any potential organics, before a final acetone pump to remove further organics and promote a quick drying time. Afterwards, by pumping air through the tubing to remove and evaporate the acetone it was predicted the pump would be cleaned. When testing this however, regardless of the pump time of air through the system (tested up to 12 hours overnight) there would be remaining acetone in the system which could be detected in subsequent Raman scans. Using isopropyl alcohol as a substitute for acetone resulted in the same situation whereby, residual Raman peaks were clearly remaining in the subsequent scans. Since most of the samples are water based, contamination of water is inconsequential, so instead of ending with an acetone/air cycle, water was continually flushed after the acetone phase. By performing Raman scans periodically during the final water flush to determine the required duration of a water flush to remove any trace of acetone in the Raman spectra, it was found that a water flush of over 45 minutes was necessary. For any reasonable use in a laboratory environment, this duration was unreasonable. Since the longest remaining contaminant signal was solely from the
acetone, and the initial aim of using acetone was for a greatly accelerated evaporation time, removing acetone completely from the procedure was acceptable. Through several test and check experiments, the finalized filling and cleaning procedure for cleaning the pump system was developed as follows:

Step 1: Circulate sample for 2 minutes.

Step 2: Circulate air for 1 minute.

Step 3: Circulate methanol for 1 minute.

Step 4: Circulate air for 1 minute.

Step 5: Circulate water for 8 minutes.

Step 6: Circulate air for 1 minute.

Step 7: If additional samples are required, go to Step 1, else completely flush with air.

This cleaning procedure was tested for CdTe NPs, a gold NP sample containing cetyl trimethylammonium bromide provided by the chemistry department, and a highly concentrated sample of PAA. In all cases, when taking a Raman scan of deionized water at the end of the cleaning procedure, no unexpected peaks were evident. However, it should be stressed that an additional cleaning procedure may need to be developed if the primary solvent is not water, since all of the tested samples were water soluble.

5.2.3- Reproducibility of Raman Spectra

To expand the use of the peristaltic pumping system with TCT into desirable scientific studies, there must be a certain level of reliability in the spectral data produced. Initially however, the main problem encountered when using the pump to fill and analyze samples within the TCT was the intensity consistency of scans taken of the same sample.
When comparing various tests there was a wide variation in resultant spectra. It was particularly evident when taking scans over relatively long periods of time (upwards of 5 minutes). To investigate this problem further, ten scans over a period of nine minutes were taken at intervals of one minute each using a 20 cm length of TCT. The sample used was simply water, and the Raman modes being focused on are in the range of 3200-3500 cm\(^{-1}\) and correlate to O-H stretching in the water molecules.\(^{38}\) As can be seen in Figure 5-2, with increased time after the filling of the TCT, the intensity of the water peak stays relatively steady for two minutes before gradually decreasing. After nine minutes of having the pump turned off, the Raman signal has fallen to only a quarter of its intensity. The shape and features of the O-H stretching remain intact, simply the intensity of the collected Raman data is changing.

Figure 5-2: Time resolved Raman scans of the O-H stretch in 20 cm of TCT over nine minutes.
This drop of intensity with respect to time is attributed to the tendency of the water surface level to gradually recede over time due to the backpressure and water seeping slowly around the rollers of the peristaltic pump. This can be visually observed through the video camera attached to the Raman spectrometer whereby the water level is clearly seen prior to the beginning of the scan, but at its conclusion, it may or may not remain. In addition to the back flow of the water, there may also be increased rates of solution evaporation when the 17 mW laser beam is focused on to a small volume of the sample.

The changing water level will cause two significant problems. Primarily, the changing level of water will cause the laser beam to change its focus onto the sample in the TCT. Due to the confocal nature of the laser system, the laser beam is focused onto a small volume of the liquid sample. If the liquid level varies enough such that the laser focus volume is not completely in the sample, the beam will begin to diverge and subsequently the amount of laser power being coupled into the waveguide will decrease. In addition to losing a certain amount of power into the sample, if the focus of the objective lens that collects light to be analyzed by the spectrometer is changing and not necessarily in or on the sample itself, the collection efficiency will drop. Secondly, all assumptions thus far into the effects of a LCW on Raman spectra have been based on the concept that the liquid in the TCT creates a perfectly flat entrance and exit surface for light in the waveguide. This is not necessarily true due to the inherent surface tension of water that will create curved facets due to a difference in molecular attractions between water molecules and the surrounding material. This curved surface can act as a type of lens and significantly change the coupling of light into the waveguide. With a perfectly
flat liquid surface, the exercise in coupling light into and out of the waveguide comes
down to numerical aperture matching between the objective lens and the waveguide
itself. For TCT filled with water ($n \approx 1.33$), it was determined that the lens with the
closest NA is the 10x lens. The fiber will have an NA of around 0.32, and the 10x has an
NA of 0.25, whereas the 50x lens has an NA of 0.75, and the 100x lens has an NA of 0.9.
It has been demonstrated that the 10x lens provides the most Raman signal in comparison
to the other available objectives (50x and 100x).\textsuperscript{56}

To counteract this inconsistency of Raman signal intensity and gradual decrease
in fluid level with respect to time, attempts were initially made to defocus the laser beam
slightly and lower it’s focus further into the core of the TCT. Once the exit facet of the
TCT had been focused on, the focus was lowered from 0.1 - 0.3 mm. When comparing
similar time resolved scans of water, this defocusing was found to provide no consistent
effects. Without reliably being able to control the surface characteristics of the water
column, the approach taken was to normalize the liquid level between scans to enhance
the reliability of data collection on identical samples. Figure 5-3 shows six spectra of
deionized water, with focus on the O-H stretch mode. Scans were taken approximately
two minutes apart, however, between each scan, the pump motor was briefly engaged to
bring the fluid level back to the facet of the TCT. When comparing the variance of
intensity of the different scans, it can be determined that the intensity values range from
3700-4100 counts, which is only a difference of about 10\% in comparison to the 75\%
drop previously encountered. The example presented in Figure 5-3 indicates the efficacy
of resetting the sample level between scans to achieve less variance between spectra. A
10\% difference between maximum and minimum was quite small when compared to the
range of other consistency tests, and through additional measurements it was determined that the intensities of Raman modes in liquid samples can be controlled to approximately +/- 15% of a mean intensity by resetting the liquid level in between consecutive scans.

![Figure 5-3: Comparison of O-H stretch mode in six different scans of water. Between subsequent scans, the pump was operated and the water surface level was restored.](image)

For increased reliability and for future spectrum gathering from samples, not only should the liquid level be normalized between scans, but also careful regard for appropriate spectrometer settings should be used. For example, the time scale of a single Raman scan can take upwards of thirty minutes depending on grating used, range of wavenumbers analyzed, accumulation time and number of averages. From the time resolved scans shown in Figure 5-2, it can be concluded that considerations should be taken in order to limit the time of a single scan to less than two minutes in order to ensure relative consistency both within the same scan and also between different experiments.
5.3- **Enhancement of Raman Signal with Length**

In a previous study comparing equivalent lengths of PCF and TCT, it was found that PCF offered somewhat enhancement of Raman signal than TCT. However, since the PCF is unsuitable for the in situ measurements using the active filling of the peristaltic pump, it is desirable to investigate the levels of Raman enhancement that TCT can offer. In Section 2.5-, Equation 2.25 was derived as the total Raman scattering power exiting the waveguide, combining this equation with the effective length equation (Equation 2.26) for a backscattered Raman spectrometer, the overall Raman power exiting a real waveguide can be determined as:

\[ P_R = P_L \cdot s \pi \frac{n_{co}^2 - n_{ci}^2}{n_{co}^2} \cdot \frac{(1 - e^{-2\alpha z})}{2\alpha} \]  \hspace{1cm} (5.3)

where \( P_L \) is the input laser power, \( s \) is a scattering coefficient, \( n_{co} \) and \( n_{ci} \) are the refractive indices of the core and cladding respectively, \( \alpha \) is the attenuation constant of the waveguide at which the laser intensity in the waveguide will have decreased by a factor of 1/e, and \( z \) is the length of the waveguide used. When studying the effect of length on Raman signal, the entire first term from Equation 5.3 can be grouped into a single constant \((k)\), creating an equation with respect to waveguide characteristics as shown:

\[ P_R = k \cdot \frac{(1 - e^{-2\alpha z})}{2\alpha} \] \hspace{1cm} (5.4)

From the equation several characteristics of the resulting length vs. power curve, can be intuitively determined. At a length of zero, there will be no Raman power, so the graph will begin at zero and increase with \( z \) towards a horizontal asymptote defined by \( k/2\alpha \). Perhaps less intuitive is that the derivative of the equation or rate of change of the
signal is dominated by exponential decay and beyond lengths of $\alpha^l$, while the signal will still be increasing, the gain offered by increasing the length is significantly less than when the LCW length is less than $\alpha^l$. At a length equivalent to $1/\alpha$, $(1-e^{-2})$ or $\sim 86.5\%$ of the maximum Raman power will be reached and will be defined as the “optimum” length of the TCT. A previous study that applied the postulations from Equation 5.4 showed initial linear enhancement at relatively small LCW lengths (only up to 30 cm). However, the experiments were not performed using the peristaltic pump system, and longer lengths were not tested and thus the exponential decay and optimal lengths were not explored completely. Experiments with regards to the changing length of the LCW were performed to further investigate the LCW pump system with respect to length.

Four different lengths of TCT were used to gather spectra from four different samples. The samples were different mixtures of ethanol and water in varying volume concentration ratios (25:1, 50:1, 100:1, and 200:1, water to ethanol solutions). The four lengths used were 20 cm, 40 cm, 117 cm, and 157 cm. Three different spectra were taken for each of the 16 combinations of lengths and concentrations. Following this, peaks were fit to the spectral range from 850 cm$^{-1}$ to 1800 cm$^{-1}$. Within this range there were six evident peaks correlating to alcohol, and on corresponding to water. The peaks for ethanol are located at approximately, 880 cm$^{-1}$, 1047 cm$^{-1}$, 1087 cm$^{-1}$, 1279 cm$^{-1}$, 1457 cm$^{-1}$, and 1488 cm$^{-1}$, and the peak for water is located at approximately 1640 cm$^{-1}$. Figure 5-4 displays a sample raw spectrum taken of the 25:1 concentration using a 20 cm TCT waveguide and Figure 5-5 shows the baseline removal and subsequent peaks fit to the same spectra.
Figure 5-4: Raw spectrum with baseline not yet removed of 25:1 water to ethanol solution obtained using a 20 cm TCT length. Peaks displayed are approximated and not yet fitted.

Figure 5-5: Modified spectrum of 25:1 water to ethanol solution with baseline removed and peaks fitted properly to the spectrum.
After fitting all spectra using the LabSpec software, the absolute amplitudes of the three of the strongest ethanol peaks (880 cm\(^{-1}\), 1087 cm\(^{-1}\), and 1457 cm\(^{-1}\) and the single water peak were tabulated for analysis. Using the curve fitting toolkit in Matlab to fit to the means of the peak amplitudes from each of the three consecutive scans, experimental values of both \(k\) and \(\alpha\) from Equation 5.4 were determined.

The fitted \(1/\alpha\) values with calculated averages and standard deviations for given concentrations and \(k\) values as determined by Matlab are shown in Table 5 and Table 6 respectively.

**Table 5: \(1/\alpha\) Values as Determined by the Matlab Curve Fitting Routine**

<table>
<thead>
<tr>
<th>Raman Peaks Fitted</th>
<th>Concentration</th>
<th>880 cm(^{-1})</th>
<th>1087 cm(^{-1})</th>
<th>1457 cm(^{-1})</th>
<th>Water</th>
<th>AVG</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25-1</td>
<td>54.35</td>
<td>55.68</td>
<td>60.06</td>
<td>57.90</td>
<td>57.00</td>
<td>4.35</td>
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<tr>
<td></td>
<td>50-1</td>
<td>80.19</td>
<td>76.28</td>
<td>84.82</td>
<td>68.45</td>
<td>77.43</td>
<td>12.01</td>
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<tr>
<td></td>
<td>100-1</td>
<td>80.00</td>
<td>101.68</td>
<td>97.28</td>
<td>81.04</td>
<td>90.00</td>
<td>19.23</td>
</tr>
<tr>
<td></td>
<td>200-1</td>
<td>186.25</td>
<td>200.48</td>
<td>202.68</td>
<td>161.13</td>
<td>187.64</td>
<td>33.10</td>
</tr>
</tbody>
</table>

**Table 6: \(k\) Values as Determined by the Matlab Curve Fitting Routine**

<table>
<thead>
<tr>
<th>Raman Peaks Fitted</th>
<th>Concentration</th>
<th>880 cm(^{-1})</th>
<th>1087 cm(^{-1})</th>
<th>1457 cm(^{-1})</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25:1</td>
<td>488.1</td>
<td>130.8</td>
<td>199.6</td>
<td>149.4</td>
</tr>
<tr>
<td></td>
<td>50:1</td>
<td>178.2</td>
<td>49.58</td>
<td>72.88</td>
<td>105.7</td>
</tr>
<tr>
<td></td>
<td>100:1</td>
<td>90.34</td>
<td>21.46</td>
<td>32.68</td>
<td>82.95</td>
</tr>
<tr>
<td></td>
<td>200:1</td>
<td>23.51</td>
<td>5.769</td>
<td>8.079</td>
<td>61.96</td>
</tr>
</tbody>
</table>

As may be expected, the absorption coefficients change primarily with respect to the change in concentration of ethanol. However, the change in absorption length and thus optimum LCW length over the four concentrations tested is quite large. Depending on the concentration of ethanol, the optimum length ranges from 57 cm to almost 190 cm. Figure 5-6 plots the change in inverse absorption coefficient with respect to ethanol.
concentration for each of the peaks. The error bars provided on the average values correspond to one standard deviation to either side of the average. Each individually fitted absorption coefficient from the separate peak amplitudes lie within the range of one standard deviation.

Figure 5-6: $1/\alpha$ (Attenuation length) with relation to concentration of ethanol in water

In addition to the change of absorption in the LCW due to the ethanol, additional changes may be occurring associated with the curvature of the liquid level in the TCT. By adding a solvent into the water, the uniform surface tension that is static in pure water will be disrupted due to interaction with the ethanol molecules. Depending on the concentration, the surface tension will change and could affect the coupling of the laser light properly into the sample.
A sample spectrum of the curve fit and the experimental data points is shown in Figure 5-7. This fit is typical of all of the other curve fits that have been created. From the analysis of the curve fits, two main discrepancies between the experimental points and the fitted curve are at the 20 cm and 40 cm lengths. In all of the analyzed data curve fits, the 20 cm length experimental data points fell below the curve, whereas the 40 cm lengths lay above the fitted curve. The curve does not appear as sharp rising in the lower wavenumbers to accommodate both the 20 and 40 cm data points. From the experimental data points, the Raman signal can be identified as reaching closer to its maximum value in shorter lengths than the $1/\alpha$ predicted by the equation.

![Figure 5-7: Sample curve fit using Matlab. The curve is the fit to the averages of the individual data points.](image)

The root mean squared deviation of each of the different fits (peak vs. concentration) is shown in Table 7.
Table 7: Root Mean Squared Deviation of the Curve Fits

<table>
<thead>
<tr>
<th>Concentration</th>
<th>880 cm(^{-1})</th>
<th>1087 cm(^{-1})</th>
<th>1457 cm(^{-1})</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>25:1</td>
<td>4594</td>
<td>1235</td>
<td>1953</td>
<td>1438</td>
</tr>
<tr>
<td>50:1</td>
<td>1699</td>
<td>472.3</td>
<td>671.6</td>
<td>973.1</td>
</tr>
<tr>
<td>100:1</td>
<td>779.7</td>
<td>202.9</td>
<td>257.7</td>
<td>742.9</td>
</tr>
<tr>
<td>200:1</td>
<td>286.6</td>
<td>92.89</td>
<td>77.02</td>
<td>740.2</td>
</tr>
</tbody>
</table>

Adding the error curves to Figure 5-7 of plus and minus one root mean squared deviation, to illustrate the range of one standard deviation is shown in Figure 5-8.

![Figure 5-8: Sample curve fit using Matlab. The central curve is the fit to the averages of the individual data points and the outer curves are illustrative of one root mean squared deviation from the fitted central curve.](image)

The error in the amplitude of the Raman peaks may not be solely attributed to differences in liquid levels in the LCW as was highlighted in section 5.2.3-. Other considerations may contribute to the error seen in the curve fits, especially in longer length LCWs. These include:

- increased bending losses due to the inability to extend 1.5 meters of fiber below the Raman microscope or along the available optical bench space
- increased probability of air pockets being trapped within the fiber

- variable backpressure due to changing length of column of water in the TCT that may cause liquid levels to change faster

The effects of increasing TCT length should theoretically always result in a gain of Raman signal, but it also may contribute to increased loss along the length of the fiber. In fact, as can be seen in the scattering of the data points in Figure 5-7 and Figure 5-8, some of the peak amplitudes gathered from the 40 cm length were greater than some of the amplitudes determined with both the 117 cm and 157 cm lengths. This discrepancy in the data with theory was evident in several of the other Raman peak and concentration combinations as well.

With such a large range of optimum lengths in comparison to relatively small changes in solvent concentration, it will be extremely difficult to determine an appropriate length suitable for all samples. In order to do so, a proper analysis of the absorption of the sample at the Raman laser wavelength would need to be performed. Albeit from a small sample variety using only varying ethanol concentrations in water, it is clear that the optimum length of the TCT fiber will widely vary depending on the sample. However, even with this wide variance, it is obvious even without fitting curves to the experimental data that there is a large gain in Raman signal when going from a 20 cm to a 40 cm TCT length, and much less of a relative increase in signal when moving to lengths beyond this point. This conclusion became abundantly clear in the comparison between the 20 cm and 40 cm lengths of 200:1 concentration of ethanol. Shown in Figure 5-9 is a spectrum of 200:1 ethanol in water, taken using a 20 cm length and shown in Figure 5-10 is a spectrum of 200:1 ethanol in water, taken using a 40 cm length.
Figure 5-9: Spectrum taken using 20 cm TCT of 200:1 water to ethanol volume ratio.

Figure 5-10: Spectrum taken using 40 cm TCT of 200:1 water to ethanol volume ratio.
When comparing the two spectra, it is easy to see that the peak of interest at 1087 cm$^{-1}$ is clearly distinct from its neighbor and the background when using the 40 cm length, however in the 20 cm spectrum, it is impossible to discern the 1087 cm$^{-1}$ peak both from its neighbor but also the noise inherent in the scan. Using 40 cm length of TCT offers enough Raman enhancement to be able to distinguish the ethanol peak at 1087 cm$^{-1}$ at low concentrations from the background of the spectrum.

As discussed previously in Chapter 4, and the evident variability of the absolute amplitude of the Raman peaks in the length comparison, for proper sample analysis, peak shifts and changes should be studied comparative to other peaks within the same scan. This effectively negates any change in background or coupling concerns since it should be applicable to the entire spectra, rather than just an individual Raman mode. To emphasize this point further, the amplitude ratios of the ethanol peaks to the water peak were compared from the previous length measurements. The averages of the individual peak ratios with comparison to water with all of the lengths combined are shown in Table 8, along with the standard deviation in Table 9, and the coefficient of variation in Table 10.

<p>| Table 8: Averages of Peak Amplitude Ratios of Ethanol Peaks to Water Peak |
|------------------------|-----------------|-----------------|-----------------|-----------------|
| Peak  | Concentrations |</p>
<table>
<thead>
<tr>
<th></th>
<th>25:1</th>
<th>50:1</th>
<th>100:1</th>
<th>200:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>880 cm$^{-1}$</td>
<td>3.045</td>
<td>1.851</td>
<td>1.109</td>
<td>0.418</td>
</tr>
<tr>
<td>1087 cm$^{-1}$</td>
<td>0.839</td>
<td>0.495</td>
<td>0.301</td>
<td>0.106</td>
</tr>
<tr>
<td>1457 cm$^{-1}$</td>
<td>1.374</td>
<td>0.777</td>
<td>0.452</td>
<td>0.149</td>
</tr>
<tr>
<td>Peak</td>
<td>25:1</td>
<td>50:1</td>
<td>100:1</td>
<td>200:1</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>880 cm⁻¹</td>
<td>0.332</td>
<td>0.171</td>
<td>0.084</td>
<td>0.036</td>
</tr>
<tr>
<td>1087 cm⁻¹</td>
<td>0.063</td>
<td>0.044</td>
<td>0.018</td>
<td>0.012</td>
</tr>
<tr>
<td>1457 cm⁻¹</td>
<td>0.061</td>
<td>0.078</td>
<td>0.041</td>
<td>0.029</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peak</th>
<th>25:1</th>
<th>50:1</th>
<th>100:1</th>
<th>200:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>880 cm⁻¹</td>
<td>10.909</td>
<td>9.253</td>
<td>7.534</td>
<td>8.518</td>
</tr>
<tr>
<td>1087 cm⁻¹</td>
<td>7.517</td>
<td>8.911</td>
<td>5.902</td>
<td>11.113</td>
</tr>
<tr>
<td>1457 cm⁻¹</td>
<td>4.443</td>
<td>10.075</td>
<td>9.184</td>
<td>19.624</td>
</tr>
</tbody>
</table>

From the coefficient of variation, it can be concluded that the peak amplitude ratios of the ethanol peaks to the water peak consistently offer a standard deviation within approximately 10% of the mean. The exception being at extremely low concentrations (in this experiment 200:1 water to ethanol concentration), it becomes difficult to discern certain peaks from the noise in the spectrum and fitting becomes problematic. The table values of the 1087 cm⁻¹ peak in the 200:1 water to ethanol ratio do not include values taken with the 20 cm length, since proper fits for this peak were unobtainable as shown previously in the comparison between the 20 cm and 40 cm lengths in Figures 5-9 and Figure 5-10.

While the PCF was found unsuitable for implementation into future in situ experiments, with TCT, the circulation was successful and could potentially be used for real time in situ monitoring of reactions or samples. The length experiments with TCT in this chapter have demonstrated that even though there is obvious error between the Matlab curve fits and the experimental data points, there is clearly an advantage to using...
a LCW of sufficient length for liquid Raman scans. While the theoretical equation given by Equation 5.4 can propose an optimum LCW length for gathering Raman data, experimental errors associated with proper coupling of light into and out of the waveguide, water level consistency, and varying levels of sample absorption cause this value to range dramatically. Along with the absolute intensity enhancement of Raman signal with length, it was also calculated that the relative peak amplitudes between the ethanol and water modes remain constant, as would be expected and required for accurate future use. The determination of a single LCW length for all Raman scans is impossible to due to the change of sample absorption, however, from this study, it appears that a 20 cm length does not provide adequate enhancement for the study of low concentration solvents in water. By using at least a 40 cm length, much improved signal to noise ratio and identification of low amplitude Raman modes can be obtained.
Chapter 6. Conclusion

6.1- Summary

The ever expanding and extremely broad field of “nanotechnology” is presently venturing forward into widespread application in industry and society. With uses ranging from consumer products to high efficiency optoelectronic devices to medical diagnostics, the use of nanoparticles is becoming commonplace. Colloidal nanoparticles in particular have proven to be particularly exciting due to characteristics such as a wide variety in material types, reduced cost of creation, and compatibility with biological systems and various substrates. However, the characterization and study of these materials in their native, liquid form is constrained by current analysis techniques that have proven unsuitable for obtaining critical information in many cases or destructive in others. Raman spectroscopy has previously been shown capable of providing desired information on colloidal nanoparticles in a liquid environment. However, the signal of Raman spectroscopy is inherently weak to the point that discerning the signal of extremely small structures in a large aqueous background is nearly impossible. To counteract this the use of liquid core waveguides has been employed. In addition to being able to properly characterize the nanoparticles, is the goal of being able to adapt post synthesis certain characteristics of the material. The colloidal growth process, while based on wet chemical techniques, is highly sensitive to changes. Adjusting the synthesis procedure in attempts to control nanoparticle characteristics can often prove challenging and time consuming. Rather, using effective tailoring post synthesis to enhance certain properties
of the material may prove much more successful. Rapid thermal annealing has not been previously applied to colloidal nanoparticles even though the use of this novel processing method is apparent in the semiconductor industry. In this thesis, the application of rapid thermal annealing to dehydrated nanoparticles has been shown to enhance semiconductor core crystallinity while at the same time preserving the optical characteristics that are also important. This crystallinity enhancement due to rapid thermal annealing has been shown reproducible through experiment repetition.

6.2- Conclusion of Results

The crystallinity of the CdTe core in the NPs was initially characterized using a novel method of Raman spectroscopy using LCWs. With the subsequent enhancement in sensitivity, a decrease in the amplitude ratio of Te-Te defect modes to an expected CdTe LO mode was documented. The change in amplitude ratio was most significant in a region of interest primarily between 200°C and 400°C processing. Since this increase of crystallinity in NPs had not been previously documented with the application of Raman spectroscopy, it was important to corroborate the postulation of an enhanced semiconductor core through other methods. As such, the use of XRD was employed that also indicated an increase in core crystallinity and prevalence of zincblende type structure with 400°C processing. In the XRD results, a diffraction feature not associated with zincblende CdTe was evident in the as-grown NP sample, however, with increased annealing temperature between 200°C and 400°C this feature was significantly reduced. While it is not known whether this feature was present due to Tellerium defects within the crystal itself or due to a partially mixed type crystal from the synthesis procedure, the
crystalline enhancement with increased temperature correlates to the results initially identified using Raman spectroscopy. Also analyzed was the effect of rapid thermal annealing on the optical characteristics of the CdTe NPs. In general, it has been seen that with conventional annealing, even below 200°C a significant reduction in PL intensity occurs. As well, higher temperature conventional annealing processes have also demonstrated the growth in size of CdTe NPs. Both the reduction of PL intensity and size growth of NPs could be potentially detrimental for integration into optoelectronic devices. However, when analyzing the effects of rapid thermal annealing, it was seen that no observable size change of the particles occurred up to a processing temperature of 600°C. This conclusion was backed by both PL and UV-vis absorption spectra as well as TEM images of the pre- and post-annealed samples. As well, using rapid thermal annealing opposed to conventional annealing allowed the samples to be processed at temperatures up to 400°C with little to no reduction in the PL intensity of the NPs. By reducing the thermal budget of the annealing process by using RTA, enhancement of the crystalline core structure can be obtained without adversely affecting the optical characteristics of the NPs.

Subsequent to the RTA experiments, a peristaltic pump was employed to allow for active circulation of a liquid sample into the core of a Teflon capillary tube (a type of liquid core waveguide). With this experimental setup, the implementation of in situ Raman spectroscopic monitoring of chemical reactions such as those associated with the synthesis of CdTe NPs is realizable. While the monitoring of a specific reaction was not performed, the enhancement of Raman signal with respect to the length of the LCW used was investigated. By analyzing the Raman spectra from four different concentrations of
ethanol in water using four different lengths of LCW, curves corresponding to the theoretical enhancement of Raman signal were fit to the experimental data. From these curves, experimental values of $\alpha$, the attenuation constant of the waveguiding system was obtained. It was determined that the attenuation constant, and subsequent “optimal length” of the LCW for Raman enhancement varied widely depending on the type or concentration of material used. No optimal length for the Raman spectroscopic investigation of an unknown material could be identified since the optical characteristics of different samples, such as the refractive index or absorption, varies too widely. However, by using the active peristaltic pumping system, a significant amount of enhancement in the sensitivity to Raman scattering events was found to occur with the use of a 40 cm LCW in comparison to a 20 cm LCW. While, further increasing the LCW length was found to provide slight signal enhancement, the effects were minimal. As such, when utilizing the developed peristaltic pump and LCW apparatus for Raman spectroscopic investigations, a LCW length of at least 40 cm should be used to ensure sufficient signal enhancement.

In summary, this thesis presents the suitable application of Raman spectroscopy to study aqueous systems in liquid core waveguides and identify crystalline changes in the semiconductor core of nanometer scale crystals.

6.3- Future Work

While the rapid thermal annealing of PAA capped CdTe colloidal nanoparticles has demonstrated enhanced core crystallinity further investigations are certainly in order. By expanding the parameter space of the rapid thermal processing through varying for example the heating gradient, overall anneal time, or annealing atmosphere, other
exciting phenomena may be discovered. Parallel to expanding the process conditions, is to analyze this process on other varieties of colloidal nanoparticles. Not only changing the semiconductor core material, but also experimenting with different capping ligands, especially those that involve conducting polymers and may be useful in optoelectronic devices such as QD-LEDs, is desirable. Ultimately, continuing efforts to create a working diode using colloidal nanoparticles and subsequently apply rapid thermal annealing to the finished device in order to investigate any changes in electronic structure could be pursued. Conventional annealing has shown improved electroluminescence in such devices, albeit, with a decrease in photoluminescence, and rapid thermal annealing has the potential to offer such an advantage without the loss in photoluminescence.

The application of the Raman spectroscopy using waveguides is also not isolated only to select nanoparticle systems. The platform can also be extended to a variety of other nanoparticles, low concentration contaminant detection in samples, or the characterization of changes in biological systems. In fact, the investigation of both DNA and also leukemia indicators with gold nanoparticles has begun and will undoubtedly require further experimentation.

Finally, making improvements on the developing sample circulation system is a work in progress. Being able to fabricate a system that allows for continual pumping of a sample while Raman scans are taking place and ensuring a flat entrance facet to the liquid would undoubtedly improve signal consistency. If properly developed, continual pumping of a sample could allow for in situ investigation of chemical or nanoparticles processes by drawing samples from a reaction container. This analysis could provide further insight into the dynamics of certain chemical reactions.
References


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