

**A Novel Synthesis and Characterization of Copper Chloride Nanocrystals in a
Sodium Chloride Matrix**

by

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Thesis Abstract

Copper chloride nanocrystals or quantum dots (QD) of various sizes are grown using simple materials, methods and standard lab heat sources, without the need for sophisticated crystal growth apparatus or control of atmosphere. The size and volume distribution of the nanocrystals is studied with small angle X-ray scattering and confirmed, along with morphology, using transmission electron microscopy. The composition of the nanocrystals is investigated using optical fluorescence emission and verified using energy dispersive spectroscopy.

Acknowledgments

There are a number of people without whom this thesis might not have been written and to them I am forever indebted. For the most important, influential and significant person in my life, I would like to thank the man who molded me into the woman I am today.

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For Bill

Table of Contents

Title Page	i
Signature Page	ii
Thesis Abstract.....	iii
Acknowledgments.....	iiiv
Table of Contents	vii
List of Figures	x
Research Proposal.....	1
Introduction.....	3
Perspective	3
Solid State Chemistry.....	4
Materials and Methods.....	5
Synthetic Methods.....	5
High Temperature	5
Liquid Phase.....	7
Gas Phase	7
Collidal Synthesis.....	9
Characterization	10
Crystallographic	10
Crystalline Materials	11
Unit Cell	11
Classification.....	12
Lattice Systems	13
Point Groups.....	13
Optical.....	14

Photoluminescence.....	15
SAXS.....	17
TEM	18
EDS	19
Production.....	20
Czochralski	20
Bridgman.....	22
Semiconductors	22
Carriers in Semiconductors	24
Doping.....	25
Dopant.....	26
Quantum Confinment.....	28
Experimental.....	30
Quantum Dots	30
Non Toxic Quantum Dots	33
Copper Chloride Quantum dots	33
Simple Growth Technique	35
Argonne and Brookhaven National Laboratoies.....	39
Results and Discussion	40
Photoluminescence	40
SAXS.....	42
TEM/EDS.....	54
Applications	59
Computing.....	60
Solar Cells	60

Biology	61
Light Emitting Diodes	62
Conclusions	63
References	65

List of Figures

Figure 1: CdSe QD Characterization	16
Figure 2: SAXS Schematic	18
Figure 3: Exciton Production	24
Figure 4: Quantum Confinement	29
Figure 5: CdSe under incadescent	31
Figure 6: CdSe under Uv, 312nm	32
Figure 7:CuCl under UV, 312nm	34
Figure 8: Three Fisher Burners	36
Figure 9 AutoCad Drawing Reaper	37
Figure 10 Reaper Data	38
Figure 11 Z3 Peak.....	41
Figure 12 PL output CuCl in NaCl	42
Figure 13: CuCl QD under incadescent	43
Figure 14: Reciprocal Space	45
Figure 15: Kossel Lines	46
Figure 16: SAXS Plots	48
Figure 17: Bessel Function w/Lg QD representaion.....	49
Figure 18: Bessel Function w/Med QD representaion	50
Figure 19: Bessel Function w/Sm QD representaion.....	51
Figure 20: Size & Volume Distribution Plot.	52
Figure 21: Size & Volume Distribution Plot Lg QD	53
Figure 22-26: Sample Degradation	54-56
Figure 27: TEM Micrograph	58
Figure 28: EDS Peaks.	59

Research Proposal

The objective was to produce non-toxic copper chloride nanocrystals or quantum dots from safe, common materials. Due to the low toxicity, ease of use, safe disposal, high availability and low cost, sodium chloride was selected as the substrate to form a host crystal with copper as the dopant. As the focus was primarily on the tunable, visible-spectrum photoluminescent properties of quantum dots, we intended copper to form the well documented “color center” point defect in the sodium chloride matrix. We intended this color center defect to mimic the photoluminescent behavior of a quantum dot. This research project would require Small Angle X-Ray Scattering analysis at Argonne National Laboratory’s Advance Photon Source to confirm the presence of quantum dots in Cu doped NaCl samples produced by our novel synthesis. The X-ray energy available at the APS is particularly useful since SAXS samples can be left large enough for spectrophotometric experiments. Together, the observed shifted photoluminescent output and the SAXS determined radius will provide empirical evidence of excitonic quantum confinement in CuCl QD's. Unlike other methods, the materials used in this QD synthesis are perfectly safe, highly available, cost effective and environmentally friendly. The reagents are inexpensive and the synthesis requires only an appropriate heat source, a crucible, a small quantity of salt and a small piece of copper. The technique requires no special skills and no control of atmosphere. The synthesis is fast, requiring only as much time as is needed to melt the NaCl, introduce copper and cool the product. The product exhibits high fluorescence intensity quantum yield which is easily stimulated with mild, inexpensive light sources. To the best of our knowledge, this is the first demonstration of a fast, simple, inexpensive synthesis of non-toxic CuCl QD's in a NaCl matrix. There are

a myriad of important applications for the product: water soluble non-toxic fluorescent tags; optically based temperature probes; optical switching; solar absorption enhancement; and undergraduate Physical Chemistry instruction. This simple, safe, quick synthesis is poised to open the field of non-toxic QD production and research to every chemist in the world.

Introduction

Perspective

Historically, advances in modern solid state inorganic chemistry were driven less by academic research and more by direct need as well as advances in technology. In the nineteenth century, inorganic chemistry helped solve the challenges facing the development of technology of photography (Housecroft and Sharpe 2005). The industrial revolution was fueled by the ability to produce steel and the need for national security drove Henry Bessemer, a British inventor, to advance the field of metallurgy (Byers 1917).

Modern electronics were made possible by advances in crystal growth (Jaeger 2002). The list of advances brought about by scientists working with inorganic materials is extensive, impressive and includes many significant achievements including the production of aluminum, lasers, magnets, superconductors, ceramics, semiconductors and optics. With this rich history of embracing the entrepreneurial and pioneering spirit, inorganic chemistry has become synonymous with problem solving and practical applications across many fields.

Advances in the field of solid state chemistry often lead to major advancements in the characterization of solid state materials in a circular fashion. The production of X-rays, an inorganic achievement in itself, led to the founding of the field of crystallography (Housecroft and Sharpe 2005). Crystallography is now a principle method of inorganic solid state materials analysis and the de facto standard for the elucidation of crystal

structure. The development of the laser and advances in semiconductor materials like aluminum doped gallium indium arsenide and other metal oxides led to advances in testing and detection such as the photo-multiplier tube, the photodetector and highly sensitive techniques like modern Raman spectroscopy (Hook 2010). Perhaps most profound has been the advances in the growth of pure material crystals like silicon, advances in deposition of single layers of crystals or films, one on the other, and the ability to selectively add impurities to these assemblies. Each of these lead to major advances in semiconductor technology and the computer based world of today. Simply put, advances in the inorganic chemistries of the solid state led to even greater advances in developing the inorganic chemistry of the solid state and may be responsible for propelling the human race forward more so than any other field.

Solid State Chemistry

The discipline of solid-state chemistry focuses on the study of the synthesis and characterization of solid phase materials. The methods used during synthesis, characterization and practical application of these materials, which often are non-molecular crystalline solids, bridge many disciplines including crystallography, electronics, mineralogy, materials science, optics and physics, to name even a few. As necessity is the mother of invention, contemporary solid-state chemists tend to focus on the synthesis and characterization of novel materials that have potential for practical application. The pursuit of novel materials that exhibit interesting and useful properties, such as semiconductor quantum dots and their non-toxic counterparts, is no exception.

Materials and Methods

Synthetic Methods

In consideration of the vast array of inorganic substances now known, including those which feature non-molecular structures, heavy atoms and ionic bonding, a wide array of methods are needed for various inorganic preparations. Some inorganic systems, such as eutectic alloys, can be manipulated at or near room temperature and often use techniques and apparatus similar to those in the general chemistry and organic chemistry laboratories. Most inorganic compounds however, such as many pure metals, ionic solids and ceramics require more exotic conditions. These sometimes esoteric inorganic synthetic conditions can generally be grouped into three categories- those involving high temperatures, those in the liquid phase and those in the gas phase.

High Temperature

For some preparations involving ionic solids, many metals and ceramics use high temperature methods. For example, bulk ionic solids such as sodium chloride, a focus of this work, may be brought into the molten phase using a crucible placed within a muffle or tube furnaces, both of which are typically capable of maintaining temperatures up to 1000 °C . For other higher melting point solids, furnaces with high-temperature refractory and heating elements made from special alloys may be employed.

For the most demanding applications such as purification of silicon ingots, inductive heating is used. In this method a heavy gauge coil of copper wire is wound into several

loops and placed around the sample or crucible. A high-power radio frequency generator then drives the coil with an alternating current which induces a powerful magnetic field (Hook 2010). The magnetic field in turn generates powerful instantaneous currents within the sample. These currents within the sample produce the heat needed for the synthetic conditions which frequently may be 2000 °C or more.

Many inorganic compounds have been made with reactants in the molten phase or from the melt. In this method reactants are typically placed in a crucible or boat, which is a small ceramic or metallic vessel which resembles its namesake. The crucible is heated using appropriate means, the reaction of interest is carried out and the product is cooled and allowed to crystallize. Annealing, or subsequent heat treatment, may also be carried out to impart desired attributes such as particular crystal phases and degrees of hardness. Volatile and gas sensitive inorganic reactions may be sealed into quartz ampoules which have been evacuated and back-filled with appropriate blanket or reactive gases (Hook 2010).

The highly specialized apparatus and exotic conditions used in many inorganic synthetic procedures are prohibitive for entry into new fields of research. Much of the work performed by the authors cited in this work takes place in just such highly specialized and expensive exotic apparatuses. As the research goal includes attention to reducing barriers to new research efforts, careful attention was paid at all phases of the work to keep costs to a minimum by creatively recycling defunct instrumentation, mimicking the functionality of expensive apparatus with a suitable inexpensive substitute, developing homebuilt apparatus creating workarounds to complex synthetic processes and using inexpensive reagents capable of producing results.

Liquid Phase

Preparation of inorganic products from the liquid phase has become an accepted practice for production of large single crystals. A typical liquid phase experiment is one where crystalline product amasses slowly by precipitation. Techniques of this type are commonly used to produce large, high quality crystalline structures. One such technique is the hydrothermal method. In this method a supersaturated aqueous solution of the species of interest is heated and pressurized in a sealed vessel known as an autoclave. By introducing a seed crystal from above on a rotating platform and controlling the temperature, pressure and movement of the seed crystal, extremely large crystals can be produce (Pierret and Neudeck 2003).

Other methods, such as spray hydrolysis, may also use organic solvents. In dissolving the species of interest in the organic solvent, nebulizing the solution and passing the vapor through a tube furnace with a carrier gas, small crystals are created. Organic solvents may also be used in the same manner as aqueous solutions in a hydrothermal process.

Researchers often shy away from using the hydrothermal and spray pyrolysis techniques when using organic solvents due the inherent risks of fire and explosion.

Gas Phase

Many inorganic compounds can be created in the gas phase with reactive gases such as oxygen, chlorine and iodine. These reactions are often carried out in a quartz tube furnace. A quartz tube furnace features a large quartz tube, typically two to three inches in diameter and three to four feet in length which is open on both ends, positioned in the

bore of a furnace which is designed to accommodate the tube exactly. The furnace produces heat from electrical current passed through heating wires coiled and embedded in refractory material. The tube may be sealed from atmosphere, evacuated or flushed with any number of lab gases. Tube furnaces are commonly used for inorganic synthesis as they are capable of controlling the atmosphere around the reaction.

Another gas phase reaction is the transport reaction. In this technique, reagents are placed in one region of a tube and reactants in another. Each region of the tube may be subjected to different temperatures depending on reaction conditions. Using a small amount of transport gas the vaporized reagents react in the gas phase and condense along a thermodynamic gradient. This method typically produces small quantities of highly purified product in the form of single crystals which are ideal for use in crystallographic analysis (Pierret and Neudeck 2003).

In a similar technique, bulk metallic copper is placed in one region and single crystals of sodium chloride are placed in another region. Chlorine is used as the carrier gas. The technique is carried out by heating copper in one region of the tube and producing a thermodynamic gradient favoring the condensation of vapor phase copper ions into sodium chloride crystalline matrixes. This technique, though effective, requires expensive tube furnaces, atmosphere control and expensive lab gases. One of the research goals outlined in this work is the reduction or elimination of expensive apparatus and gases.

Colloidal Synthesis

Traditionally, semiconductors are synthesized from precursor compounds dissolved in solutions. There are three areas to the synthesis of colloidal quantum dots; precursors, organic surfactants, and solvents. Large scale production of quantum dots use the colloidal synthesis and many of these QDs are made of binary alloys such as cadmium selenide, cadmium sulfide, indium arsenide, and indium phosphide. However, some quantum dots can be made from ternary alloys; such as cadmium selenide sulfide (Murray, Kagan and Bawendi 1993).

In colloidal synthesis, monomers are created when the precursor compound is chemically transformed. This occurs when the compounds are heated to very high temperatures. The monomers are considered to be supersaturated and where the nanocrystal growth can start. A critical factor in nanocrystal growth is the temperature during the growth process. Temperatures need to be high enough to create the monomers but low enough to promote crystal growth. An important factor is the concentration of the monomers. There are two different types of the growth process, focusing and defocusing (Peng and Peng 2002). If the concentration is very high with respect to the critical size, the nanocrystals neither grow nor shrink and result in small crystal growth. This size distribution in the focusing process produces almost all monodisperse particles. This technique is most effective when the monomer concentration is such that the average nanocrystal size present is always slightly larger than the critical size (Yin and Alivisatos 2005). As the concentration of the monomer becomes lower and lower the critical size becomes larger than the average size present, and the distribution defocuses as a result of Ostwald

ripening (Peng and Peng 2002). Ostwald ripening is when small crystals are re-deposited onto larger crystals.

Characterization

Crystallographic

Since the development of the field in the mid twentieth century, crystallography has flourished to become a primary means of the physical characterization of inorganic substances. Many solid state inorganic reactions produce crystalline and polycrystalline powders. For these, powder-based X-ray diffraction (XRD) is most useful. In this technique, X-rays are impinged upon a sample and diffracted by the long range order of electrons in the crystalline arrangement. Detectors scan the space opposite the sample exposure and collect patterns of diffracted radiation. This diffraction pattern is processed and compared against the signatures of known crystalline phases which are typically contained in a software library.

Another version of XRD is tailored for analysis of larger crystals of a millimeter or two in each dimension. Superb analytical quality is readily achieved using this non-destructive technique which is in most ways functionally identical to its powder counterpart. As the long range order of the crystals studied with this technique is on a much larger scale, greater sensitivity and highly robust structure information is collected. Careful analysis of single crystal material usually leads to publishable quality data and definitive crystal structures.

X-ray diffraction techniques are highly useful but detecting the dopant-level concentrations of quantum dots, particularly those embedded in another crystalline matrix, is very challenging. Typically the extremely small signal produced by the nanocrystalline quantum structures is nearly extinguished in the noise floor. However, some authors have had success demonstrating nanostructures within crystalline matrices. This work produces crystalline nanostructures which are highly dispersed in the crystalline matrix of another material. Signal strength has shown to be low and requires a more powerful and sensitive analytical method to produce publishable data.

Crystalline Materials

Inorganic chemists are frequently interested in materials that are crystalline in nature. These materials are those in which a particular arrangement of atoms or molecules forms a structure known as a unit cell which repeats in some series of arrangements to form long range order. In understanding unit cells, the arrangement of atoms, scientists can derive the properties of a crystalline material as a whole.

Unit Cell

Unit cells are described by three parameters, a , b , and c , which describe the length of three conjoined edges of the unit cell as well as three angles denoted α , β , and γ which describe the angular relationship between the edges. These unit cell parameters define and describe the crystalline systems. In a simple cubic crystal system, the focus of this

work, the conjoined edges are equivalent in length and the angles are orthonormal, which is to say $a = b = c$, and $\alpha = \beta = \gamma = 90^\circ$ (Massa 2000, Housecroft and Sharpe 2005).

Unit cells are the smallest possible unit of the crystal which features all of the symmetry elements of the crystalline structure. In possessing all the symmetry elements of the long range structure, a collection of unit cells, through some combination of symmetry operations such as translation, rotation, reflection and inversion, create the long range order of macromolecular crystalline solids. This understanding of the unit cell is frequently all that is required to explain many physical properties of crystalline solids (Massa 2000, Housecroft and Sharpe 2005). This work focuses in part on what effect occurs by substituting one element for another in a unit cell.

Classification

The most important property of a crystal is its intrinsic symmetry. What is meant by symmetry is that under certain 'operations' the crystal remains unchanged (Housecroft and Sharpe 2005). Crystals have translational symmetry. This is where a move of one cell in each of three axis directions restores the structure, but some crystals have other symmetry elements as well. For example, rotational symmetry is rotation of specific angle like; 90° , 120° , and 180° that restores the structure. Mirror symmetry is the reflection across a plane that restores the structure. If all the intrinsic symmetries are discovered a complete classification of the crystal is said to be made (Massa, Housecroft and Sharpe 2005).

Lattice Systems

The way to describe the lattice system in a crystal structure is through the grouping of the axial systems. As mentioned earlier, α , β , and γ describe the angular relationship between the edges of the crystal system. These angles will represent the three axes in the geometrical arrangement of a crystal. There are seven lattice systems and six crystal families. In this work, the cubic lattice system is the observed crystal system. The cubic system is the most straightforward of the systems and has the symmetry of a cube. This means that the rotational axes are orientated such that all four threefold rotational axes which lie along the body diagonals of the cube are 109.5° with respect to each other. The other six lattice systems are hexagonal, tetragonal, rhombohedral, orthorhombic, monoclinic and triclinic (Massa 2000, Housecroft and Sharpe 2005).

Point groups

The crystallographic point group of a system is a shorthand notation which reflects the relevant symmetry elements of a crystalline system. Where the mathematical group comprising of the symmetry operations leaves at least one point unmoved and that leave the appearance of the crystal structure unchanged. These symmetry operations include

- Reflection, which reflects the structure across a reflection plane
- Rotation, which rotates the structure a specified portion of a circle about a rotational axis
- Inversion, which changes the sign of the coordinate of each point with respect to a center of symmetry or inversion point
- Improper rotation, which consists of a rotation about an axis followed by an inversion.

rotation axes (proper and improper), reflection planes, and centers of symmetry are collectively called the symmetry elements. There are 32 possible crystal classes. Each one can be classified into one of the seven crystal systems (Massa 2000, Housecroft and Sharpe 2005).

Optical

Color is one of the first properties that can be observed when looking at quantum dots. However, it is the intrinsic energy within the material that defines the color of each quantum dot. Therefore, quantum dots of different colors are observed even though they are made up of the exact same materials. It is important to remember that the color of the quantum dots is directly related to the energy levels of that particular group of nanocrystals. The energy levels within quantum dots are determined by the crystals bandgap. Generally speaking this is the energy in a substance between the valance band and the conduction band. Understanding how electrons interact and get excited will help explain bandgaps more thoroughly. Negatively charged subatomic particles that surround an atom are called electrons. When electrons move together in the same direction they will cause an electric current. We can think of these electrons as being in an array of different states, which include their energy level, momentum and spin with the differing probabilities for being in any state. Since, two electrons can never be in the same state then one of the variables has to be different. The laws of quantum mechanics state that some states are forbidden and some are possible. The states that are possible are called

bands and the states that are not possible form an area between those bands, which are called bandgaps (Bastard, Mendez, Chang, Esaki 1982 and Hook 2010).

For transparent materials it is often possible to obtain valuable structural and electronic configuration information from the usual optical techniques. The interaction of light with the sample can reveal, among other things, band energies, transition states and offer insight into crystal structure. In the case of semiconductors, characterization can obtain valuable structural and electronic UV/VIS spectra (Bastard, Mendez, Chang Esaki 1982 and Hook 2010),

Photoluminescence Spectroscopy

The property most desirable in quantum dots is their ability to release photons in a photoluminescent process. When a sample is excited by laser light that has photon energy higher than the bandgap of the sample, electrons will be excited from the valence band into the conduction band leaving a hole behind in the valence band. Photoluminescence (PL) from a direct bandgap semiconductor occurs when a free electron and hole relax to the bottom of the band, and consequently recombine and emit a photon. The energy of the emitted light, the PL, which involves the transition of free electrons from the minimum of the conduction band to the maximum of the valence band, is simply the bandgap energy.

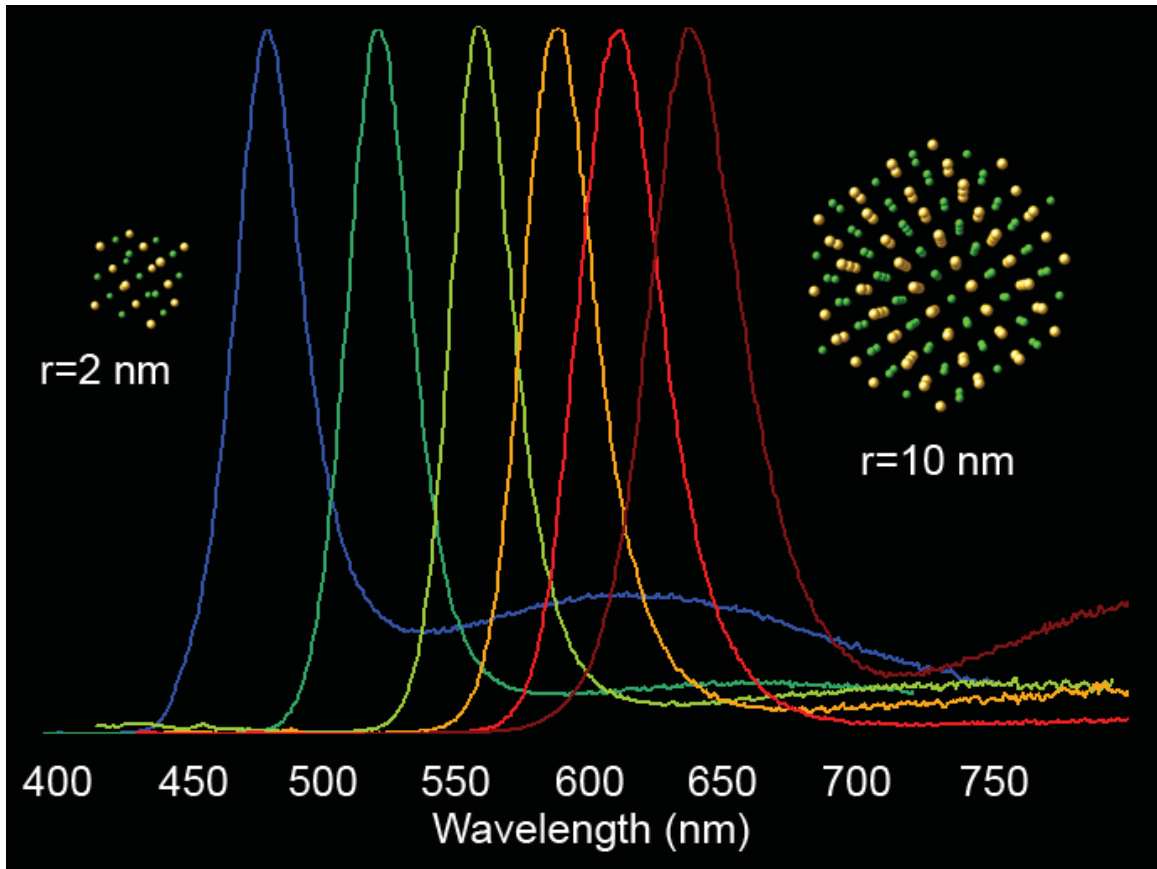


Figure 1 CdSe QD Characterization

Photoluminescence also affords researchers insight into the electronic states and quantum configuration of the quantum dots. Perhaps most interesting is the fact that the size of a quantum dot can be determined from the photoluminescent output of the dot. As seen in Figure 1, the color of the QD corresponds to the wavelength of that particular color. The size of the crystal confines the exciton which in turn changes the bandgap. In measuring the wavelength of the light emitted one can calculate the size of the crystal which produced the light.

SAXS

Small-angle X-ray scattering (SAXS) is a crystallographic technique where details regarding the size, shape and distribution of ordered structures as small as a few nanometers can be revealed. The process relies on the elastic scattering of sub-nanometer X-rays from samples with limited long range order. Just as diffracted X-rays create a pattern based on long range order, scattered X-ray patterns contain information about short range order such as shape, size and dispersion. A typical SAXS analysis reveals structural information from regions as small as a single nanometer to those over one hundred nanometers or more. Variations of the technique can resolve regions down to a single atom or molecule and up to several hundreds of nanometers. Order beyond this size is large enough for less expensive X-ray diffraction techniques.

One primary drawback of the SAXS technique is the need for highly energetic monochromatic X-ray sources and highly advanced instrumentation. Although there are small, self contained SAXS instruments available, accurate analysis of very small regions of order requires an expensive relativistic particle accelerator to generate a sufficient intensity and quality of X-rays.

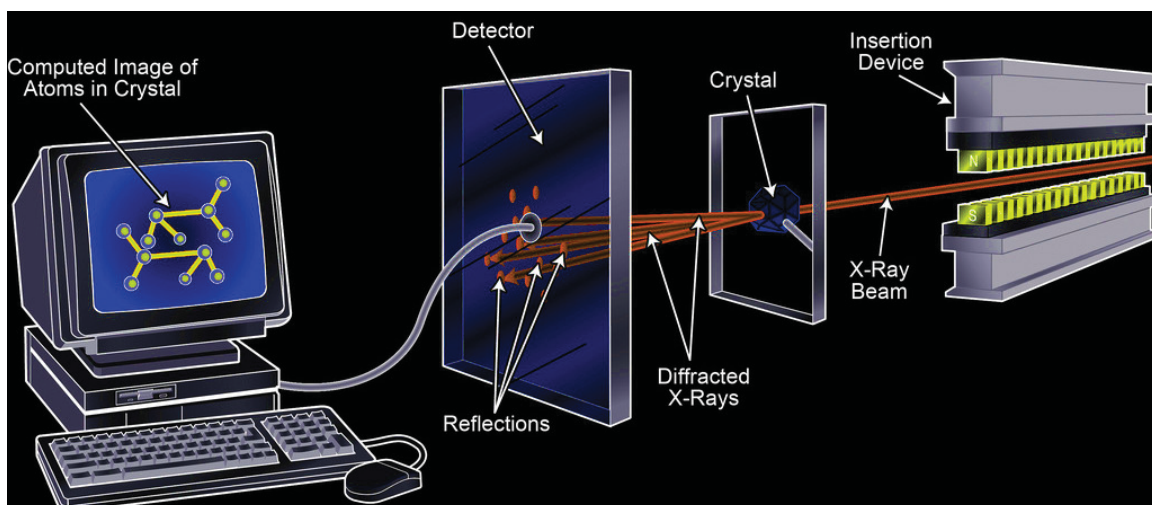


Figure 2 SAXS Schematic (<http://www.flickr.com/photos/advancedphotonsource/sets>)

Figure 2 represents a typical X-ray scattering experiment. The synchrotron X-rays are produced at the insertion device and directed to the sample. The atoms in real space scatter or diffract the X-rays into a pattern in reciprocal space on the detector. The data from the detector is typically collected and processed by computer.

TEM

Transmission electron microscopy (TEM) is a microscopy technique where a beam of electrons is transmitted through a thin sample. Images are formed from the interaction of the electrons transmitted through the sample; the image is then magnified and focused onto an imaging device, such as a fluorescent screen, or a CCD camera (Williams and Carter Barry 2009).

TEMs have the ability of imaging at a considerably higher resolution than light microscopes; this is due to the de Broglie wavelength of electrons. Allowing the user to

see very fine details even as tiny as a single column of atoms, this is thousands of times greater resolution than the smallest resolvable object in a light microscope (Williams, Carter and Barry 2009). The TEM allows major analysis to take place in a wide range of scientific disciplines, for example both the physical and biological sciences. TEMs have been used to in cancer research, virology, materials science as well as pollution and semiconductor research (Williams, Carter and Barry 2009).

The contrast in low magnification of the image is caused by the absorption of the electrons in the sample; the thickness and composition are also a factor. The contrast in higher magnifications is caused by complex wave interactions; this modulates the intensity of the image, requiring skilled analysis of observed images (Williams Carter Barry 2009).

Different modes of the TEM allow scientists to better understand their samples and to possibly learn their chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

EDS

Energy Dispersive X ray Spectrometry (EDS) uses a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements ($Z < 10$) (Williams, Carter and Barry 2009). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X - ray spectra. Quantitative analysis, determination of the concentrations of the elements,

involves measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition (Williams, Carter and Barry 2009). By scanning the beam in a television like raster and displaying the intensity of a selected X - ray line, element distribution images or 'maps' can be produced. Also, images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected (Williams, Carter and Barry 2009).

Production

The production of quantum dots is a process in which excitons need to be confined within the semiconductor material. There are several ways that this confinement can take place. Most quantum wires, wells and dots are grown by advanced epitaxial techniques but some quantum dots are produced by chemical methods, ion implantation, or in nanodevices made by state-of-the-art lithographic techniques (Delerue 2004).

Czochralski

The Czochralski process is essential in the growth of large ingots, or boules, of single crystal silicon used in semiconductor manufacturing; such as silicon, germanium and gallium arsenide, and metals like palladium, platinum, silver, gold, salts, and synthetic gemstones. This process was named for the scientist who discovered the method in 1916,

Jan Czochralski, while studying the crystallization rates of metals (Emtsev, Boris, Gagik, Kryhkov, Misiuk, Londos and Potsidi 2005).

It is very important that the highest grade of materials is used in semiconductor manufacturing. Therefore, the highest purity semiconductor-grade silicon impurities, of just a few parts per million, is used. The silicon is melted down in quartz crucibles and dopant atoms such as boron or phosphorus are added to the molten intrinsic silicon in very exact amounts. This causes the silicon to change to either the n-type or p-type extrinsic silicon. The electronic properties are then useful and utilized in semiconductors. In order to melt silicon temperatures of about 1500 °Celsius are obtained. The silicon is then thoroughly melted and a seed crystal is mounted to the end of a shaft and very slowly lowered into the molten silicon but just at below the surface, then the rod rotates counterclockwise and the crucible is rotated. The rotating shaft is then very slowly drawn up and forms the cylindrical. Depending on what the manufacture is producing these boules can be from one to two meters.

In semiconductor manufacturing one highly sought after characteristics is their electronic properties. Different properties can be obtained by adding materials like phosphorus or boron to the silicon before it is melted. The added material is called the dopant and the process is called doping. This technique can be used for growing gallium arsenide, for the use of semiconductors, but typically the Bridgman-Stockbarger method is used. This is because lower defect densities can be achieved (Emtsev, Boris, Gagik, Kryhkov, Misiuk, Londos and Potsidi 2005).

Bridgman

Two very similar methods for growing single crystals were named after their inventors: Harvard physicist Percy Williams Bridgman and MIT physicist Donald C. Stockbarger. The Bridgman method is an easier and more popular way of producing certain semiconductor crystals than the Czochralski (Mikkelsen 1980). This method for making single crystal ingots is to heat polycrystalline material above its melting point and slowly cool it from the seed crystal attached to the other end of the container. This will cause the single crystal to have the crystallographic orientation of the seed material. The crystal is grown on the seed and formed all along the length of the container. The method can be carried out either in the horizontal or vertical geometry.

There are slight differences between the Bridgman and Stockbarger technique. One difference is the temperature gradient is set for the Bridgman technique and the Stockbarger technique requires manipulating the ingot through a temperature gradient in order to grow the desired single crystal (Mikkelsen 1980).

Semiconductors

A semiconductor is a material with partial electrical conductivity. Of particular interest in this work are nanometer-scale semiconductor crystals. On this small scale, quantum mechanics directly influences the behavior of the material. When electromagnetic radiation enters a semiconducting material it may interact with the matter and excite an electron to a higher energy level located in another space. The region left unoccupied by the excited electron has a lower electron density than the surrounding space and becomes

an energetic hole. The electron-hole pair remains entangled in the quantum mechanical sense and is an energy carrier capable of interacting with surrounding matter and energy. These electron-hole pairs, known as excitons, are constantly generated not only from interaction with electromagnetic radiation but also from interaction with vibrational and thermal energy as well (Pierret and Neudeck 2003). Excitons are a principle feature of semiconductors and are responsible for many of the special properties they possess. Copper chloride, the subject of this work, is a semiconductor and contains excitons.

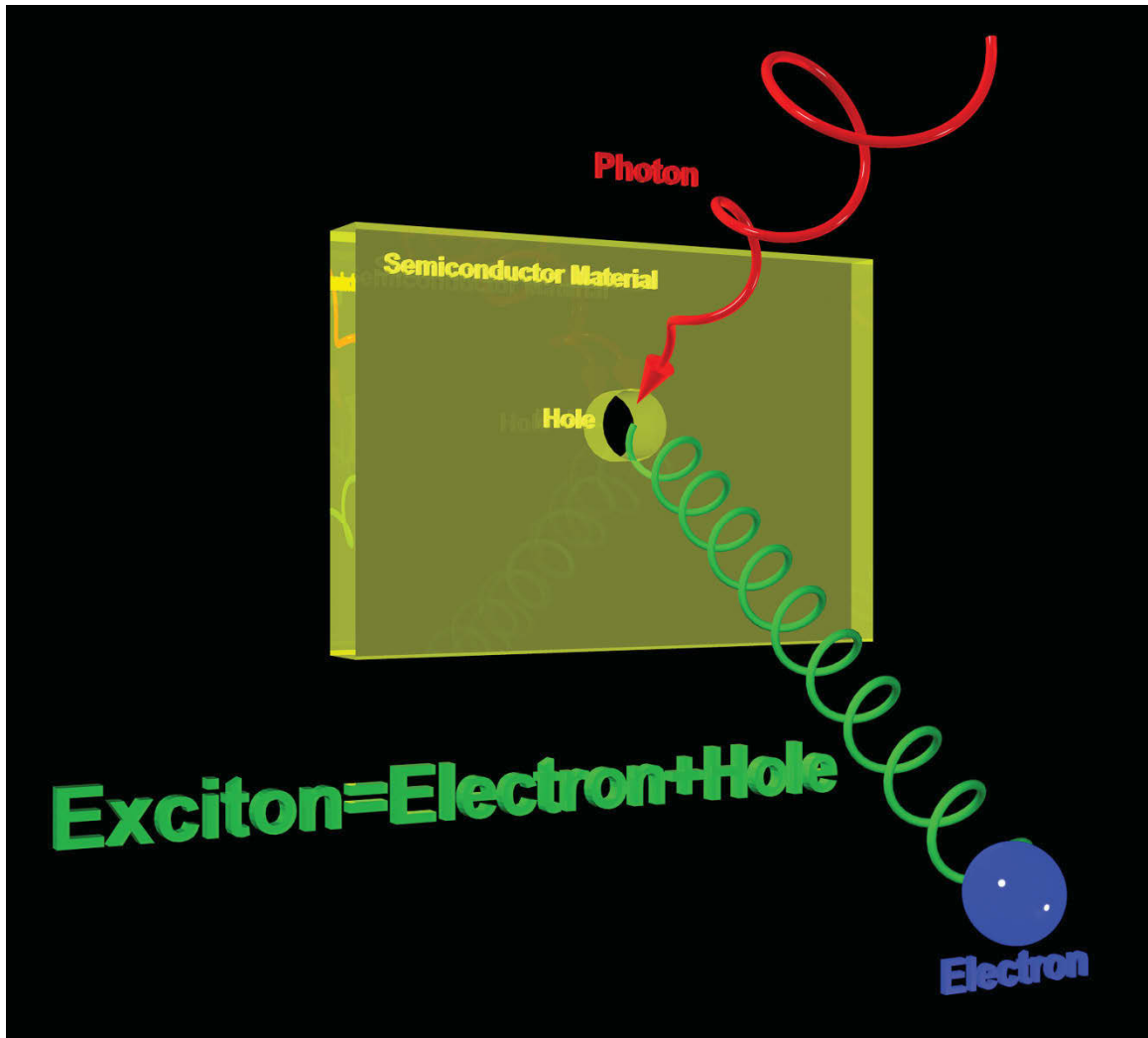


Figure 3 Exciton production

Carriers in Semiconductors

In Figure 3, when the electromagnetic radiation enters a semiconducting material it may interact with the matter and excite an electron to the conduction band. The region left unoccupied by the excited electron has a lower electron density than the surrounding space and becomes an energetic hole in comparison. These electron-hole pairs, known as

excitons, are constantly generated not only from interaction with electromagnetic radiation (Pierret and Neudeck 2003).

An exciton, or electron-hole pair, can be considered an analogy to an excited hydrogen atom and behaves in an energetically similar fashion. An electron hole pair has quantized energy states. An excited electron hole pair can absorb quantized energy. And just as the Conservation of Momentum demands the relaxation of an excited hydrogen electron produce a photon, so too does an exciton recombination (Capper, Peter and Ruduloph 2010).

Excitons are a principle feature of semiconductors and are responsible for many of the special properties they possess. Copper chloride, the subject of this work, is a semiconductor and harbors the potential for exciton production. The principle concern of this work is the production of photon emission from the quantum confined excitons within copper chloride nanocrystals formed inside a sodium chloride matrix.

Doping

Semiconductors are very useful for application in optical and electronic devices because their electronic structure is adjustable through the introduction of foreign atoms into the lattice structure. This process of selectively replacing atoms in the host lattice is called doping. The type and amount of impurity, or dopant, added to the pure semiconductor selectively modifies the electronic structure and properties of the host material in specific and predictable ways. Doped semiconductors are called extrinsic semiconductors because

their electronic properties are determined by extrinsic atoms present in the lattice (Danieluk, Bradley, Mitra, O'Reilly, Lucas, Cowely, McNally and McGlynn 2009).

Doping is most often discussed in terms of semiconductors but also finds application in materials with wider bandgaps than semiconductors (Pierret and Neudeck 2003). Many optical devices such as some solid state lasers are based on the electronic states of a single ion instead of an electron-hole pair generated in a semiconductor. The first laser, a ruby laser produced at Bell Labs, relied on chromium ions in a synthetic aluminum oxide garnet. By adding very small amounts of the impurity ion to the garnet matrix, researchers produced a viable optical device. The YAG laser is another example where only one atom percent doping with neodymium results in an infinitely large increase in optical output (Bohm 1981).

Dopants

To understand the mechanics behind this behavior it is important to understand the charge carriers responsible for it. Excitons are produced in semiconductor materials at the instant an optical photon is absorbed. The incoming photon excites an electron into a higher energy state. The absence of electron density leaves behind a hole. This electron-hole pair is known as an exciton and is the quantum structure responsible for storing the energy of the photon. At some point in time the electron relaxes back into the hole and releases the energy that was stored, often as another photon (Massa 2000). In semiconductor manufacturing understanding the desired outcomes of your semiconductor material is important. The atomic properties of both the dopant and the semiconductor are critical factors in this decision. These dopants are in two classifications; either electron

acceptors or donors. If the donor atoms are used as the dopant this will allow weakly bound valence electrons to become incorporated into the lattice structure, creating excess negative charge carriers. These weakly bound electrons can move about in the crystal lattice relatively freely and can facilitate conduction in the presence of an electric field (Schubert 2005). Some states under the conduction band edge are created and the electrons at these states can be easily excited to the conduction band, becoming free electrons, at room temperature (Schubert 2005). The electron acceptor on the other hand produces a hole. A semiconductor that is doped with the donor atoms are known as n-type and semiconductors doped with acceptor atoms are known as p-type (Bohm 1981 and Schubert 2005). The N and P are just names to indicate which charge carrier acts as the material's majority carrier (Schubert). For example, the pure semiconductor silicon has four valence electrons. In silicon, the most common dopants are IUPAC group 13 (commonly known as group III) and group 15 (commonly known as group V) elements. Group 13 elements all contain three valence electrons, causing them to function as acceptors when used to dope silicon. Group 15 elements have five valence electrons, which allow them to act as a donor (Schubert 2005, Pierret and Neudeck 2003). Therefore, a silicon crystal doped with boron creates a p-type semiconductor whereas one doped with phosphorus results in an n-type material. In this work we present a sodium chloride matrix that has been doped with copper from the bulk solid state. The copper is introduced into molten sodium chloride and incorporated as ions in the lattice structure as condensation and recrystallization occurs.

Quantum Confinement

When electrons and electron holes are being forced into a dimension that approaches a critical quantum measurement, called the exciton Bohr radius this effect is the quantum confinement effect. To better understanding the idea of quantum confinement, we can think of a substance confined to a region in space. This is just like an exciton confined inside a quantum dot. As seen in Figure 4, by taking two figures, we represent the same volume. The height of the cylinders represents the energy. As well the height of the cylinder is a function of the base size when the volume is held constant. For the same quantity of substance to occupy the volume above a smaller base, the height of the cylinder must increase. This is an analogy of the three dimensional particle in a box and exactly describes how a wave confined to a smaller space has greater energy. In the exact same fashion, an exciton confined to a smaller crystal will have a higher energy than an identical exciton free to roam a larger volume.

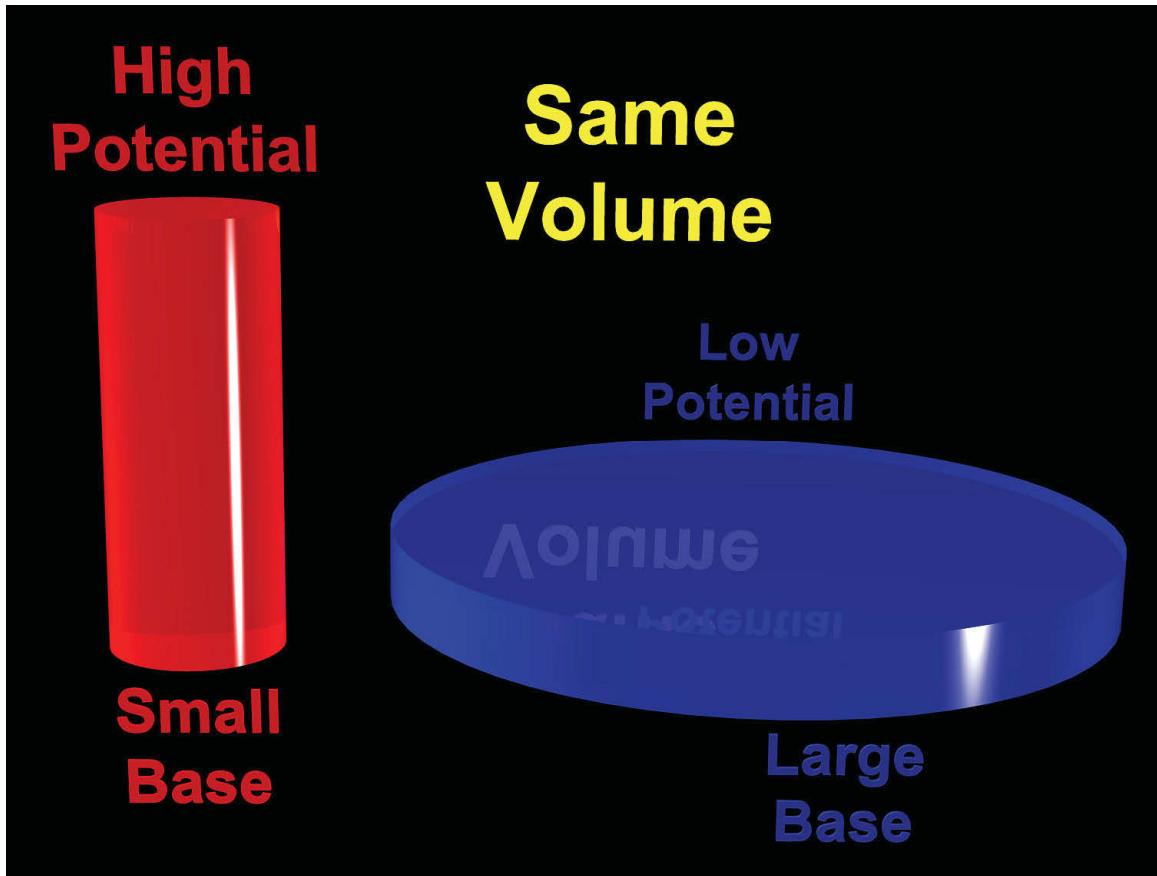


Figure 4 Quantum Confinement

The electronic and optical properties of materials are affected by size and shape. Well established technical achievements including quantum dots were derived from size manipulation and investigation for their theoretical corroboration on quantum confinement effect (Voge, Welsch and Wallentowitz 2001). The major part of the theory is the behavior of the exciton ensembles more like an atom as its surrounding space shortens. The properties of semiconductors can be changed if the quantum confinement of the electron and the electron hole are manipulated and is quickly becoming a means to many new electronic structures (Voge, Welsch and Wallentowitz 2001).

Experimental

Quantum Dots

Quantum dots are tiny crystals of semiconductor material that exhibit special optical properties which are attributed to their size. As semiconductors, the materials from which quantum dots are made contain pairs of electrons and holes. However, as opposed to the bulk semiconductor material, the quantum dots serve to confine the electron-hole pair to a tiny physical space and in all three dimensions. The effect of this confinement is an alteration of the quantum mechanical properties of the semiconductor. The confinement of the electron hole pairs, which are known as excitons, produces unique optical properties of quantum dots such as shifted fluorescence output. These quantum confinement effects are observed in systems typically comprised of anywhere from several hundred to several thousand individual atoms and an overall crystal dimension of a few nanometers. In Figure 5, a typical quantum dot system comprised of cadmium selenium nanocrystals, which we produced during the course of this research, and are shown here under incandescent light. In Figure 6, the broad spectrum ultraviolet illumination on a Fotodyne Transilluminator with a peak wavelength of 312 nanometers. The confinement of excitons within the tiny crystals is responsible for the altered electronic properties of quantum dots. This means the smaller the size of the crystal the larger the band gap becomes. In smaller crystals the fluorescence shifts from the red side of the scale toward the blue. The impact of quantum confinement of the excitons within the semiconductor is evident in this shifting photoluminescent output of the quantum dots under ultraviolet illumination.

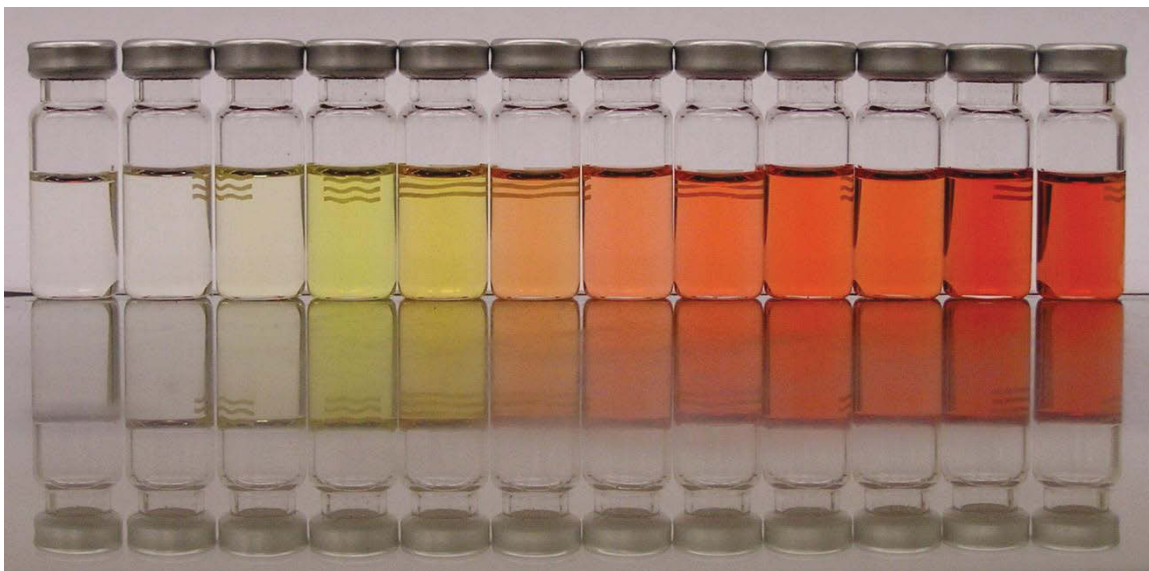


Figure 5 A typical CdSe QD system under incandescent light

Only the differing size of the crystals, from a radius of about 1.6 to 5.0 nanometers, changes the color. It is this ability to “tune” the photochemical properties of quantum dots by growing nanocrystals of differing size but from the exact same material that makes them attractive for use in chemical labeling, solar energy collection and a host of other applications. However, the highly toxic nature of the compounds required for synthesis of quantum dots is a major disadvantage. Like many of the elements used in semiconducting materials, cadmium and selenium are toxic even in minute quantities. The desire to produce safe, inexpensive, easily synthesized, non-toxic quantum dots then became the impetus for this research.

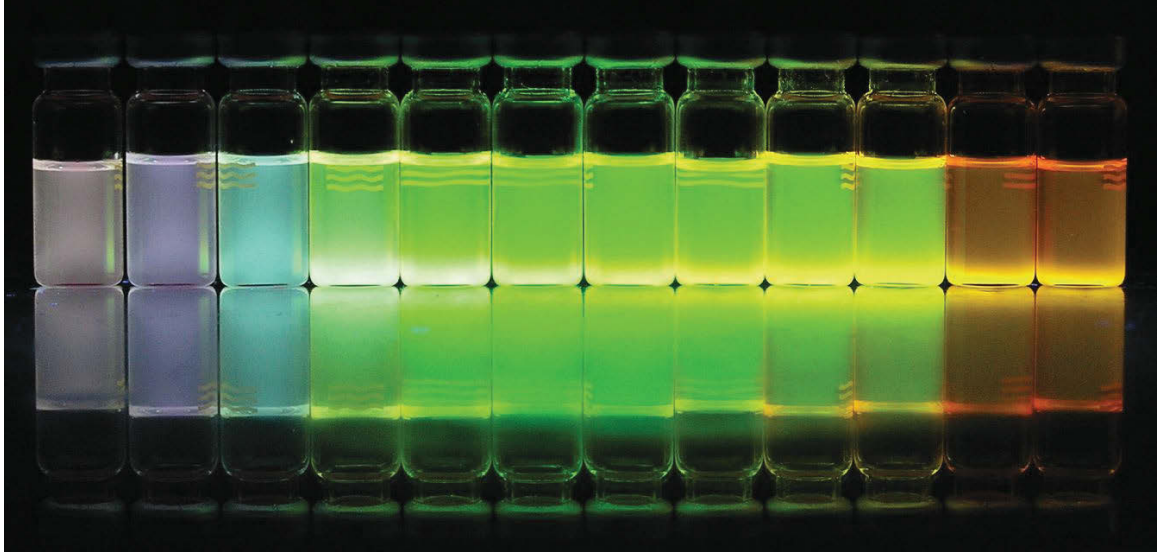


Figure 6 A typical CdSe QD system under UV, 312 nanometers

Seen here in Figure 6, it is apparent that the quantum dots in the violet and purple vials are smaller than the quantum dots in the yellow and orange vials. The excitons in the smaller crystals are confined to a smaller volume and represent a larger amount of energy. The excitons in the larger crystals are free to roam a larger volume and represent a smaller amount of energy. That is why they turn from violet, to blue, to green, to yellow, to orange and to red. The crystals are bigger and bigger in each case. It is important to realize that all the crystals are made of the exact same material. Only the size of the crystals causes the color change. The advantage of quantum dots is that multiple bandgaps can be produced from the exact same material by producing different size crystals. A disadvantage is that quantum dots are typically not soluble in water, a condition needed for biological use, and the materials used to produce them are frequently toxic (Masumoto and Ogasawara 1999). The focus of this work is to overcome these limitations and produce a fluorescent quantum dot that is water soluble and non-toxic.

Non-Toxic Quantum Dots

Cadmium-free quantum dots are also called (CFQD's). The use of heavy metals in consumer goods is quickly becoming a growing concern and many large industrial countries are banning the use of these heavy metals. This would put a restriction on cadmium based quantum dot applications. There is a wide open market for the commercial application and implementation for heavy metal-free quantum dots. A new type of CFQD can be made from rare earth (RE) doped oxide colloidal phosphor nanoparticles. (Reed 1993) This is different than semiconductor nanoparticles, RE's excitation is due to UV absorption of host material, which is the same for different RE doped materials using the same host. Therefore, the emission will depend on the type of RE. Since the synthesis is aqueous based the problems with water solubility were eliminated and therefore are of viable use in biological applications. However, there are some reports concerning the use of phosphor nanoparticles on biological targeting and imaging. (Howarth, Liu, Puthenveetil, Zheng, Marshall, Schmidt, Wittrup, Bawendi, Ting and Nat 2008)

Copper Chloride Quantum Dots

Copper chloride (CuCl) is a semiconductor material which is non toxic and exhibits properties that make it useful as a quantum dot. CuCl has an exciton Bohr radius of about 0.7 nm, an exciton binding energy of 190 meV and a cubic unit cell. (Krandold, Kriesen Haselhoff, Weber and Goerigk 2003) In addition, CuCl has known exciton structures, namely $Z_{1,2}$ and Z_3 in the ultraviolet region of the spectrum (Krandold, Kriesen,

Haselhoff, Weber and Goerigk 2003). These features make CuCl a candidate material for making quantum dots. CuCl is non-toxic and is highly soluble in water, both conditions needed for use in biological systems. CuCl is so soluble it must be protected from water. By embedding the CuCl quantum dots in another crystalline matrix, one that is transparent, non-toxic and also water soluble, the CuCl crystals are protected. Based on prior works sodium chloride (NaCl) is an excellent choice as a host (Itoh, Iwabuchi and Kataoka 1988). By introducing copper as a dopant material into NaCl, CuCl quantum dots are created within the protective matrix. Here in Figure 7, one can see the various PL outputs.

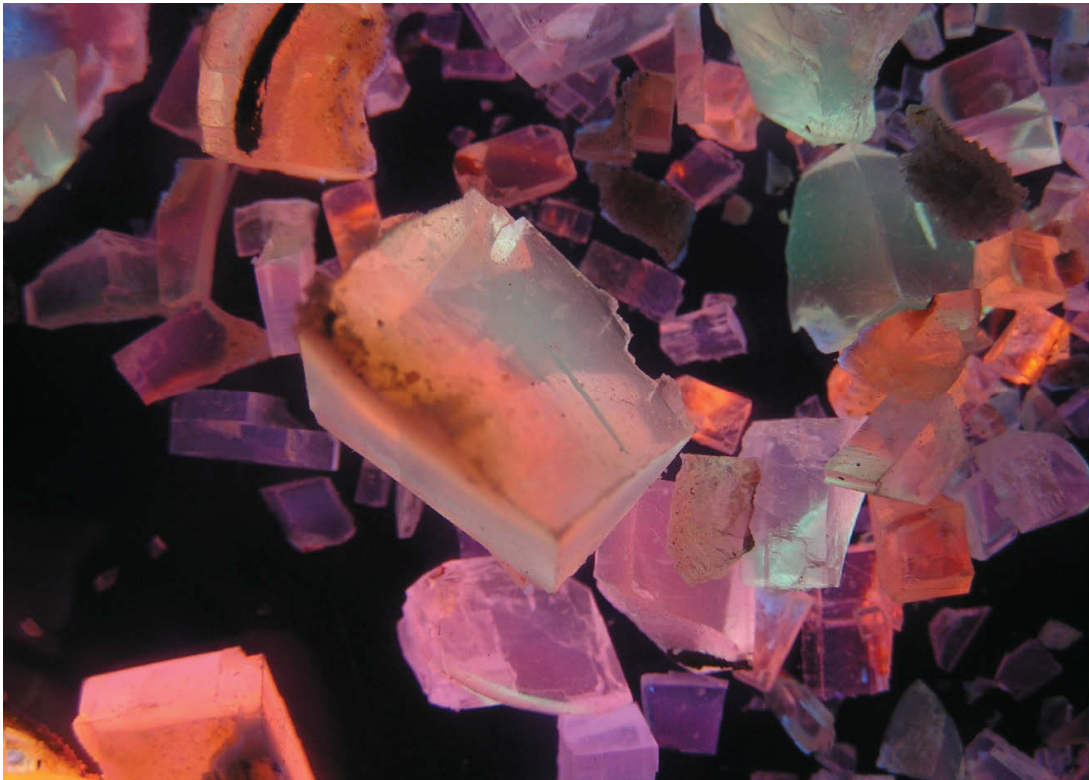


Figure 7 CuCl QD in a NaCl Matrix under UV 312 nm

Simple Growth Technique

Sodium chloride melts at around 801 °C, a temperature reachable with common lab gases such as methane or propane, we chose to create the copper-doped sodium chloride compound from the melt or molten state. Figure 8 shows an assembly of three Fisher burners. We found that 10 g of ACS grade sodium chloride became molten in a covered 25mL ceramic crucible in about ten minutes. Once molten, we introduced copper from the solid phase as a wire bent into various shapes. Using tongs we stirred the molten sodium chloride with the copper wire and observed the immediate removal of copper oxides from the surface of the wire by the molten sodium chloride. After stirring we removed the copper wire and covered the melt to allow any product that crystallized during the stirring process to melt. After a short period, we removed the crucible from heat and allowed it to cool in air over a period of about twenty minutes. We removed the cooled product by placing the crucible upside down on the bench and striking it with a hammer until the product fell free or the crucible was broken apart.

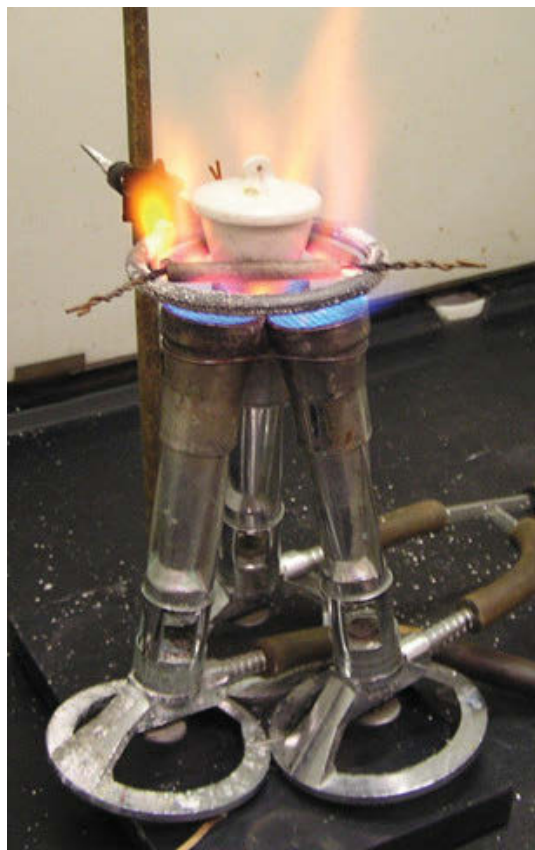


Figure 8 Three Fisher Burners

Figure 9 shows how our technique for melting sodium chloride evolved during the research. One of the primary goals of this research is cost control and simplification. With those in mind, a custom built computer controlled furnace (named the Reaper) was built from commercially available silica refractory bricks capable of resisting heat to 1200 °C, an industrial computer interfaced to an IBM-PC for data acquisition and control and quartz heating elements harvested from a consumer toaster oven as a heat source.

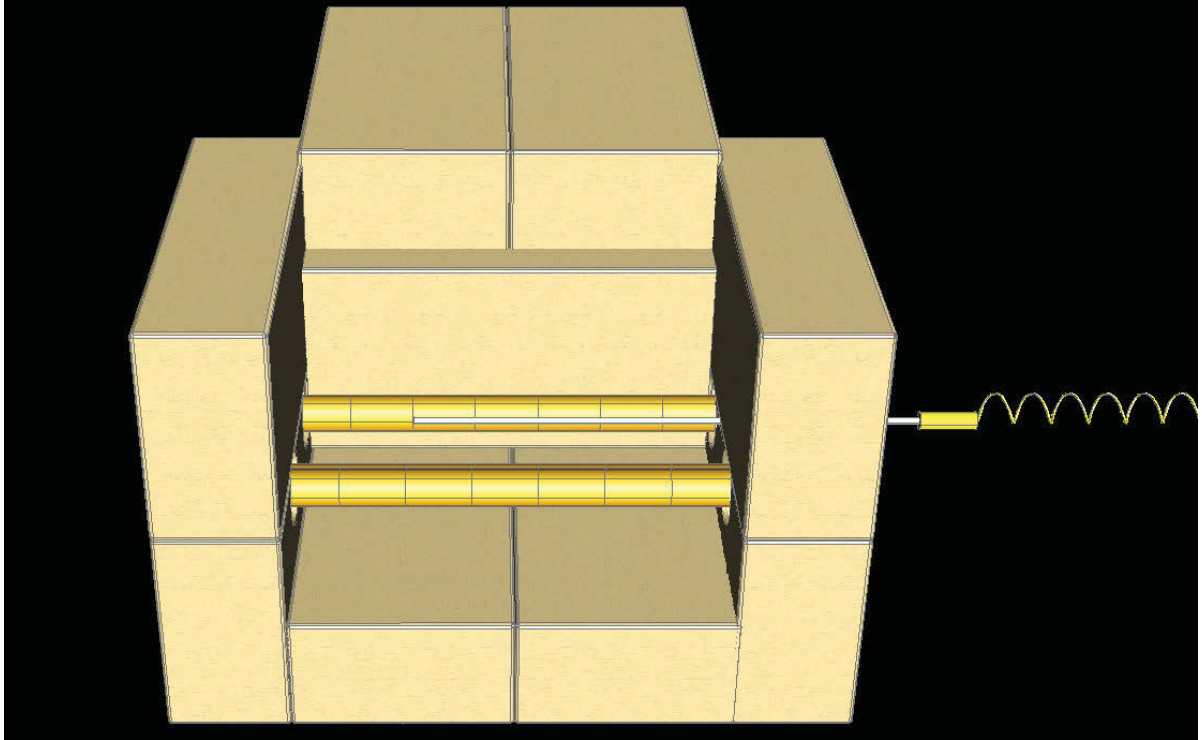


Figure 9 AutoCad drawing of the Reaper

As the furnace evolved so did the procedure for producing well resolved crystals with the desired PI outputs. Figure 10 shows an automated program file for the Reaper. In order to achieve well resolved crystals we discovered our cool down period needed to occur over a long time period. Therefore, we varied times and temperatures over dozens of experiments and found that a cool down period taking approximately two days gave us the best crystals as well as all the optical properties we desired.

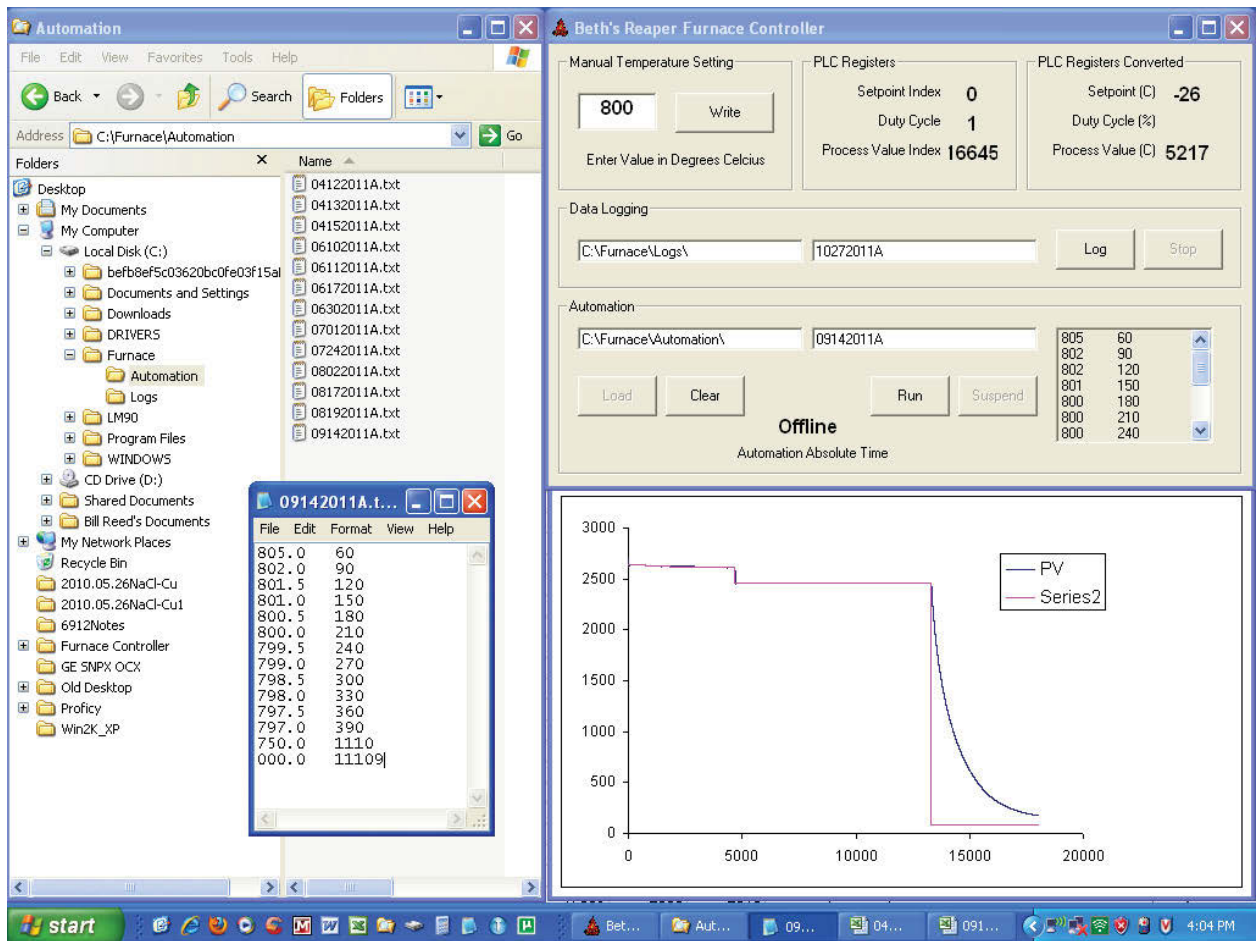


Figure 10 Automated program file for the Reaper

Many experiments were run using varying amounts of copper wire; the shape of the wire was altered, (spirals, helices, pieces, etc.); time of sodium chloride exposure to copper; amount of sodium chloride; heating and cooling rates; temperatures; and other variables.

Argonne and Brookhaven National Laboratories

Based on a literature review, several pieces of empirical information are typically used to fully characterize quantum dots of this type of nanocrystal size, as determined by SAXS, TEM imaging and photoluminescent behavior as well as through the usual spectrophotometric techniques. In order for these types of characterizations to take place we required the aid of large facilities like the Advance Photon Source (APS) at Argonne National Laboratory (ANL), as well as the Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory (BNL). To obtain access to these facilities, proposals needed to be written and submitted for review. The scoring process is on a scale from 1-5, where 1 is the best and 5 is the worst. Note: anything above a 2.6 does not get time at either of these facilities. A committee of specialized national laboratory scientists reviews the proposals and score the proposed research based on scientific or technical importance. As one of the primary researchers, William Reed and I set out to author well written proposals with enough scientific and technical importance to gain access to these two facilities. It was my honor to work alongside William Reed. We authored and submitted several proposals. This work was fortunate enough to benefit from access to both facilities. Both facilities scored our proposals very highly. Our Argonne proposal scored a 1.6 and Brookhaven a 1.1. As well as our research was said to be highly innovative and of great importance. Also mentioned, this research is an open-ended project that will either launch a new application for nanoscience research or will clearly impact one of the outstanding problems in the field of nanoscience.

Our research includes the results of analysis from both the Advanced Photon Source at Argonne National Laboratory in Chicago, Illinois and the Center for Functional Nanomaterials at Brookhaven National Laboratory in Long Island, New York.

Results and Discussion

Photoluminescence

Observed photoluminescence of the product was quantified using a custom, purpose-built spectrometer. The sample was secured in an Abbess Instruments transverse optical cryostat charged with liquid nitrogen, equipped with dual orthogonal sapphire windows and maintained at 90 K as indicated by properly calibrated, dual silicon diode cryosensors coupled to a Lake-Shore 330 temperature controller.

The sample was illuminated with light from a 150 W high-pressure Xenon source profiled with 1 mm slits, passed through a .25 m folded Czerny-Turner monochromator tuned to 325 nm and focused to a spot comparable in size to the SAXS probe beam using dual cylindrical quartz optics. Fluorescence emission from the sample was collected with quartz optics placed orthogonal to the excitation source and channeled into an automated 0.85 m dual Czerny-Turner monochromator with 2400 line/mm gratings blazed for 400 nm and profiled with four sets of 1 mm slits located at the input and output of each of the monochromators. Optical signals were detected with a Hamamatsu R928 photomultiplier tube biased at 600 VDC and housed in a refrigerated enclosure at 253 K. Noise reduction was achieved using a Stanford Research Systems optical chopper operating at 1 kHz and an SR850 DSP Lock-In Amplifier.

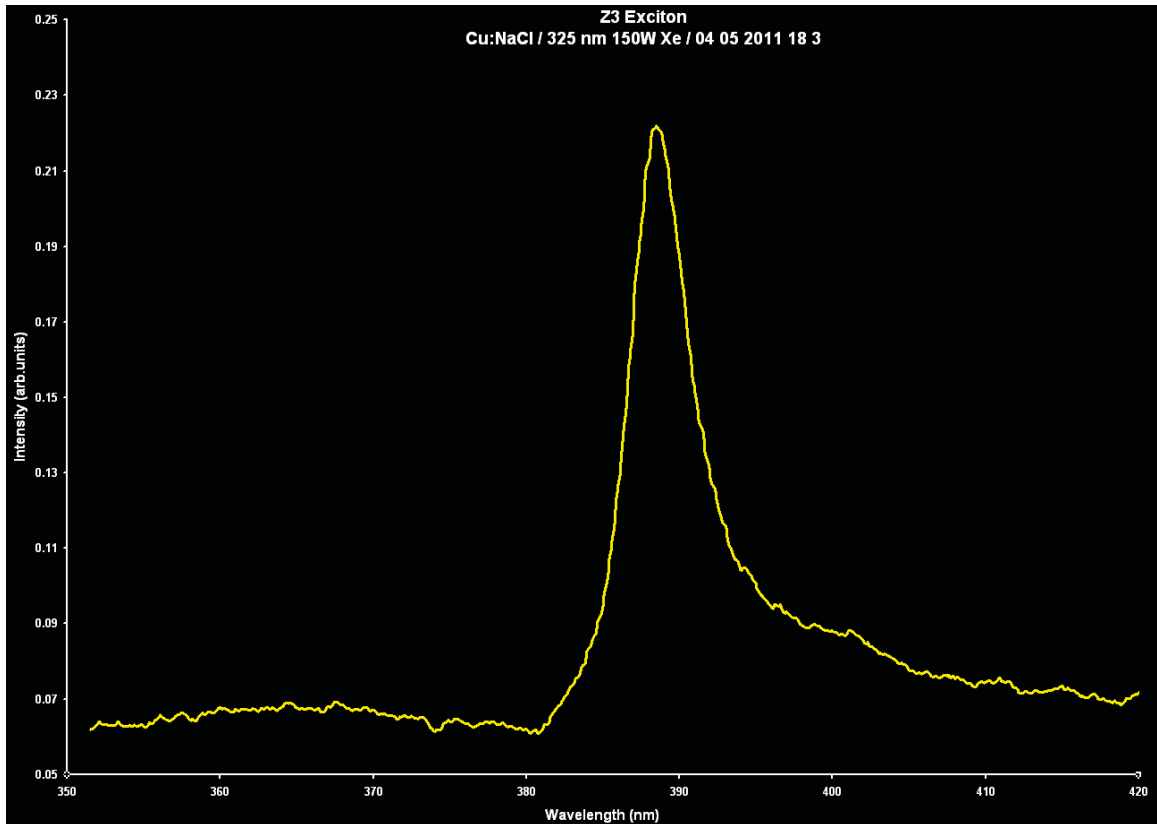


Figure 11 Z₃ Exciton Peak

As indicated in Figure 11, the collected spectrum indicated a fluorescence peak of the Z₃ exciton, a known structure present in bulk copper chloride and generally located near 388 nm. In Figure 12, various PL outputs within the system are seen. Recall that this material is all the same composition the yellow fluorescence represents larger QDs and the purple fluorescence represents the smallest QDs within our NaCl matrix.

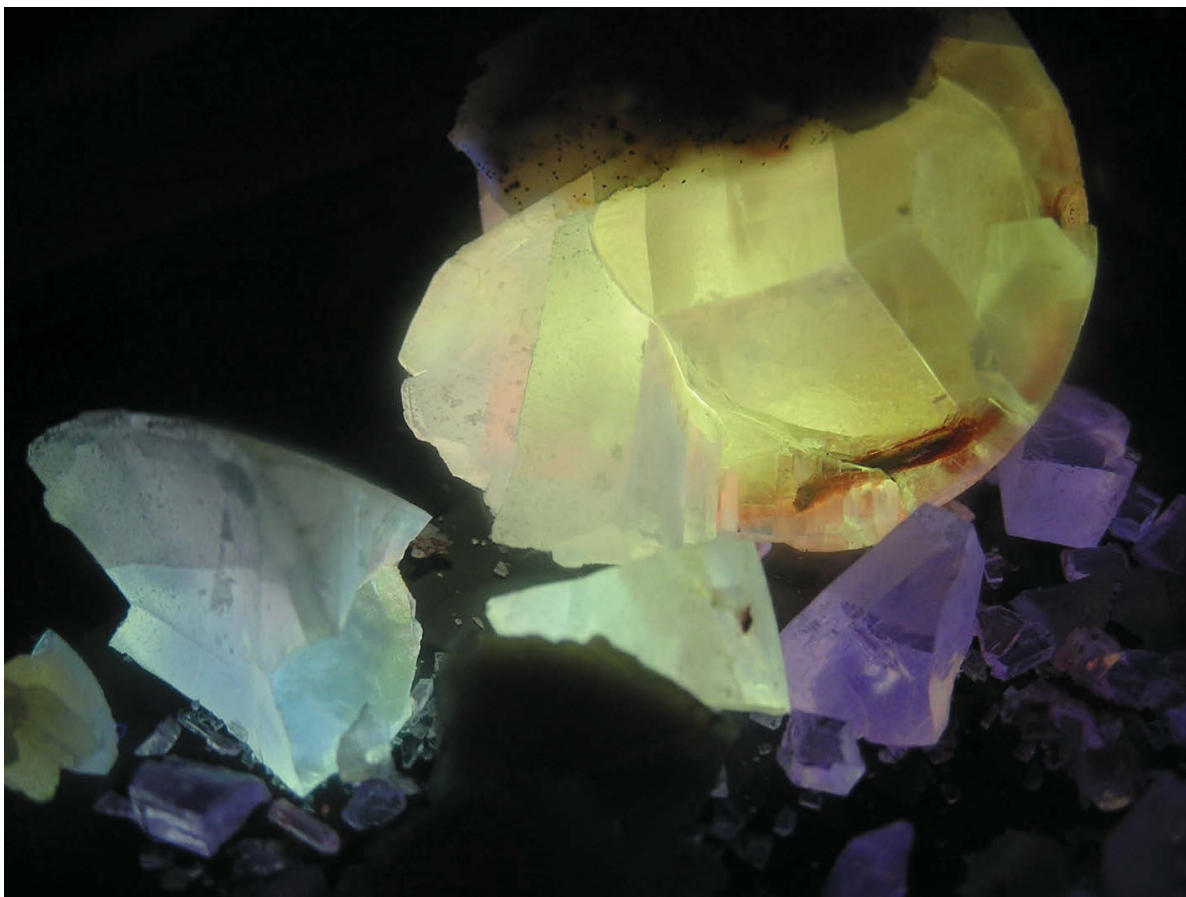


Figure 12 PL of CuCl in NaCl

SAXS

The purpose of the proposed SAXS analysis at the APS is to answer the primary research question of whether or not the Cu doped NaCl samples contain QD's. Two pieces of empirical information are needed to confirm the QD's nanocrystal size, as determined by SAXS, and varying photoluminescent behavior, as determined through the usual spectrophotometric techniques. The high quality and intensity of the APS affords the ability to perform spectrophotometric experiments on the exact same samples used for

SAXS. Together, the varying PL behavior and the SAXS determined radius of the nanocrystals provide evidence of the quantum confinement of excitons typical in QD's.

Figure 13 shows an actual sample analyzed during our last visit to Argonne National Laboratory. This is about the size of a fingernail and represents a gradient of quantum dot sizes. One can see the effect of probing the system with intense synchrotron radiation.

We probed at different regions since we have a distribution of nanocrystal sizes in different areas



Figure 13 CuCl QD in a NaCl Fingernail

The small angle X-ray scattering (SAXS) portion of the investigation was carried out at the Advanced Photon Source at Argonne National Laboratory on beamline 12-ID-B. The beam energy was approximately 12 keV and collimated to a spot size approximately 1 mm x 2 mm at the sample. A 2 cm square tantalum plate with a 2 mm central orifice was positioned immediately prior to the sample in the space between the sample and the incoming X-rays to reduce noise from air scattering. Crystalline samples were mounted in Laue configuration via Scotch tape secured across a small wire-form apparatus atop an automated two-axis stage. For further noise reduction, immediately following the sample was placed a large vacuum chamber which occupied the entire space between the sample and the detector. The detector used was a Dectris Pilatus 2M, an advanced reverse-biased silicon diode array detector with exceptionally low background noise and single-photon sensitivity, located approximately 2 m from the Laue experiment. Samples were exposed to X-ray energy for approximately 10 s and data sets were collected as rastered lines across large regions in an effort to expose nanocrystal size gradients within the parent crystal. Two dimensional diffraction images were collected in TIFF format from the detector and reduced automatically by Matlab routines. Data was further processed using Igor Pro 6.22A with software macros Nika, Irena and Indra for further reduction, analysis and presentment.

The data collected by the detector is in reciprocal space, which differs from the positions of atoms in real space. The pattern of scattering intensity can be understood from this diagram. Incident X-rays come into the real space along the vector k_i . The photon interacts with the matter and receives momentum from the lattice. This elastic process modifies the direction but not the energy of the photon.

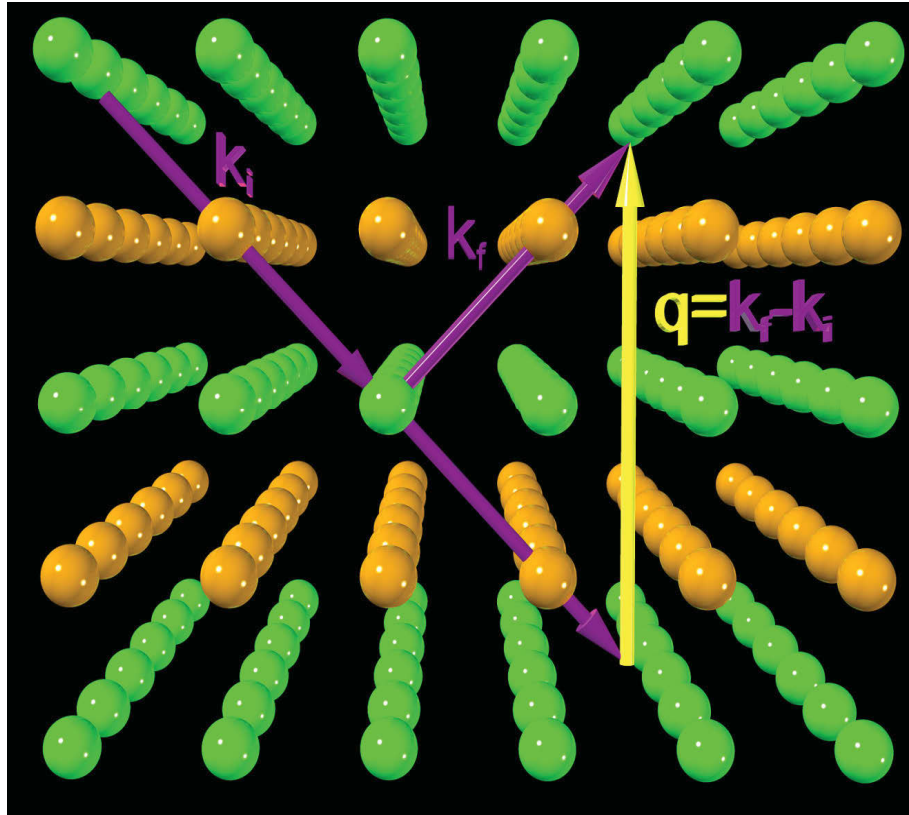


Figure 14 Reciprocal Space

The change in direction is illustrated as the photon exits along the vector k_f . The mathematical difference of the vectors k_f and k_i is the vector q which represents the momentum transferred from the lattice to the photon and becomes a lattice point in reciprocal space. A Fourier transform of the points in the reciprocal lattice yields the points in the real lattice and vice versa.

In Figure 15, radial symmetry is seen, this is a suggestion of the Kossel phenomenon and their presence is an indication of well resolved lattice planes. Kikuchi lines are seen in diffraction patterns which are caused by the diffusely scattered electrons and by the thermal atom vibrations (Kirkland 1998). Kossel lines are the equivalent to Kikuchi lines. The major characteristics of their geometry can be deduced from a simple elastic

mechanism but the dynamical theory of diffuse inelastic scattering is needed to understand them quantitatively (James 1982).

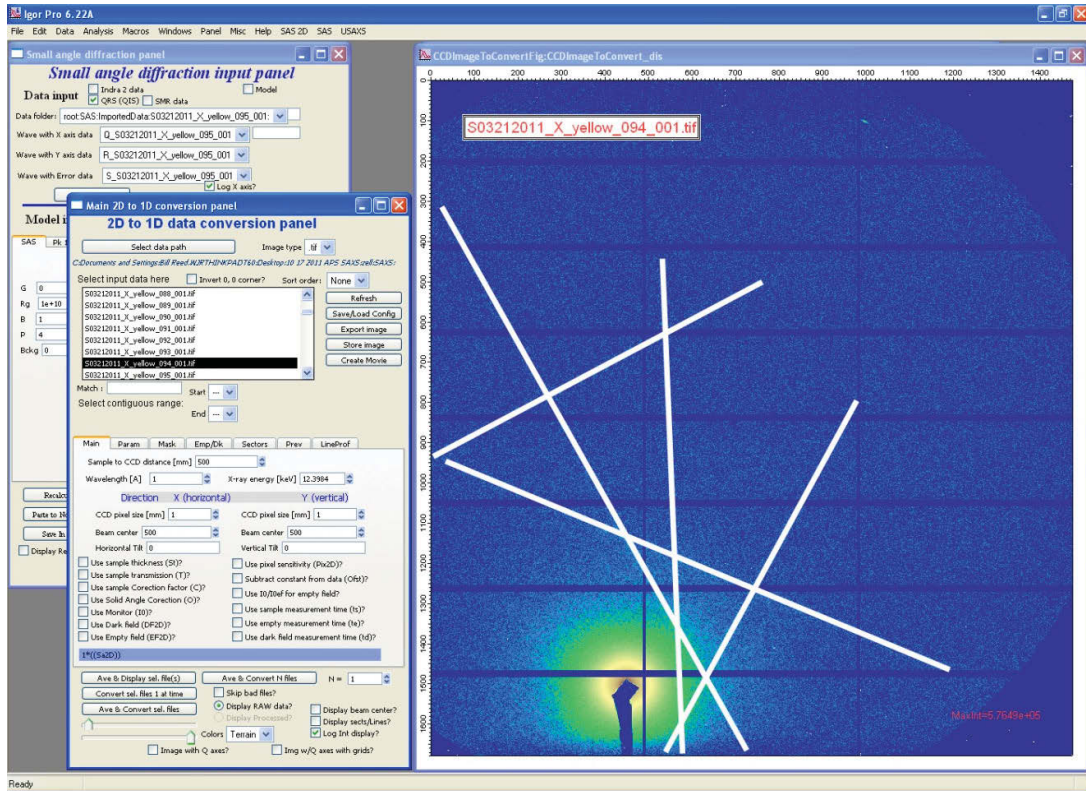


Figure 15 Kossel Lines

Once reduced the data is ready to plot in typical fashion as a SAXS plot of intensity versus q the vector mentioned in the discussion of reciprocal space.

Using software on 12ID-B, we performed a curve fit to the region of interest which is modeled as a Bessel function convoluted onto a Power-Law decay. The presence of the humps in Figure 16 indicates nanocrystals within the matrix. Focusing on the purple line, the volume distribution on that spot in the crystal indicates a four nanometer nanocrystal

diameter. Figure 16 also shows the collection of relevant SAXS plots of intensity versus q from the fingernail crystal shown previously. Each of the Bessel functions convoluted with the Power Law background indicates nanocrystals of a particular size and volume distribution in that region. In Figure 17, the red line in the upper left is the Bessel function that represents the largest nanocrystals. Figure 18 shows the Bessel functions in the middle and represents the mid-sized quantum dots and in Figure 19 the Bessel function to the lower right represent the smallest nanocrystals

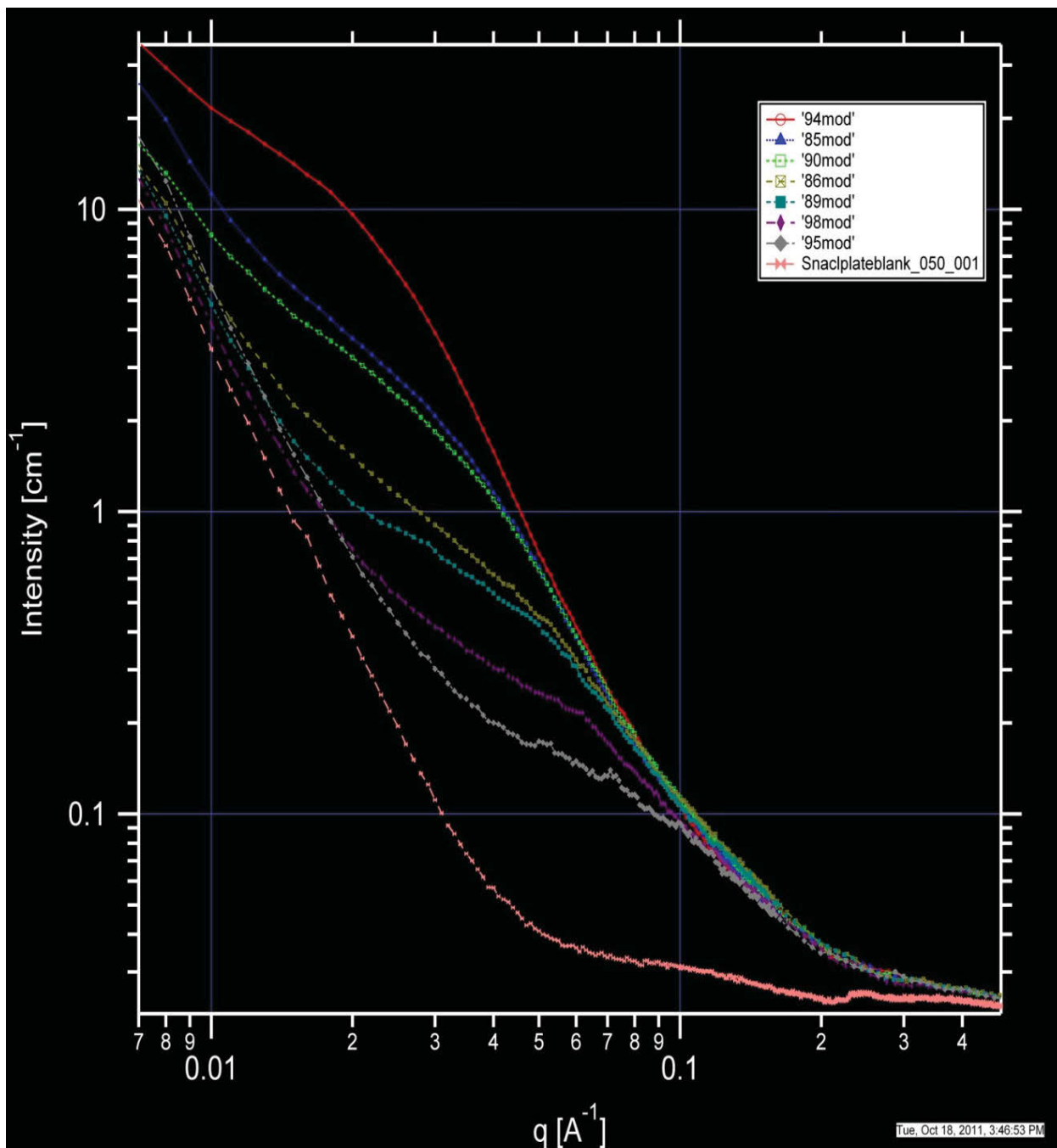


Figure 16 SAXS Plots

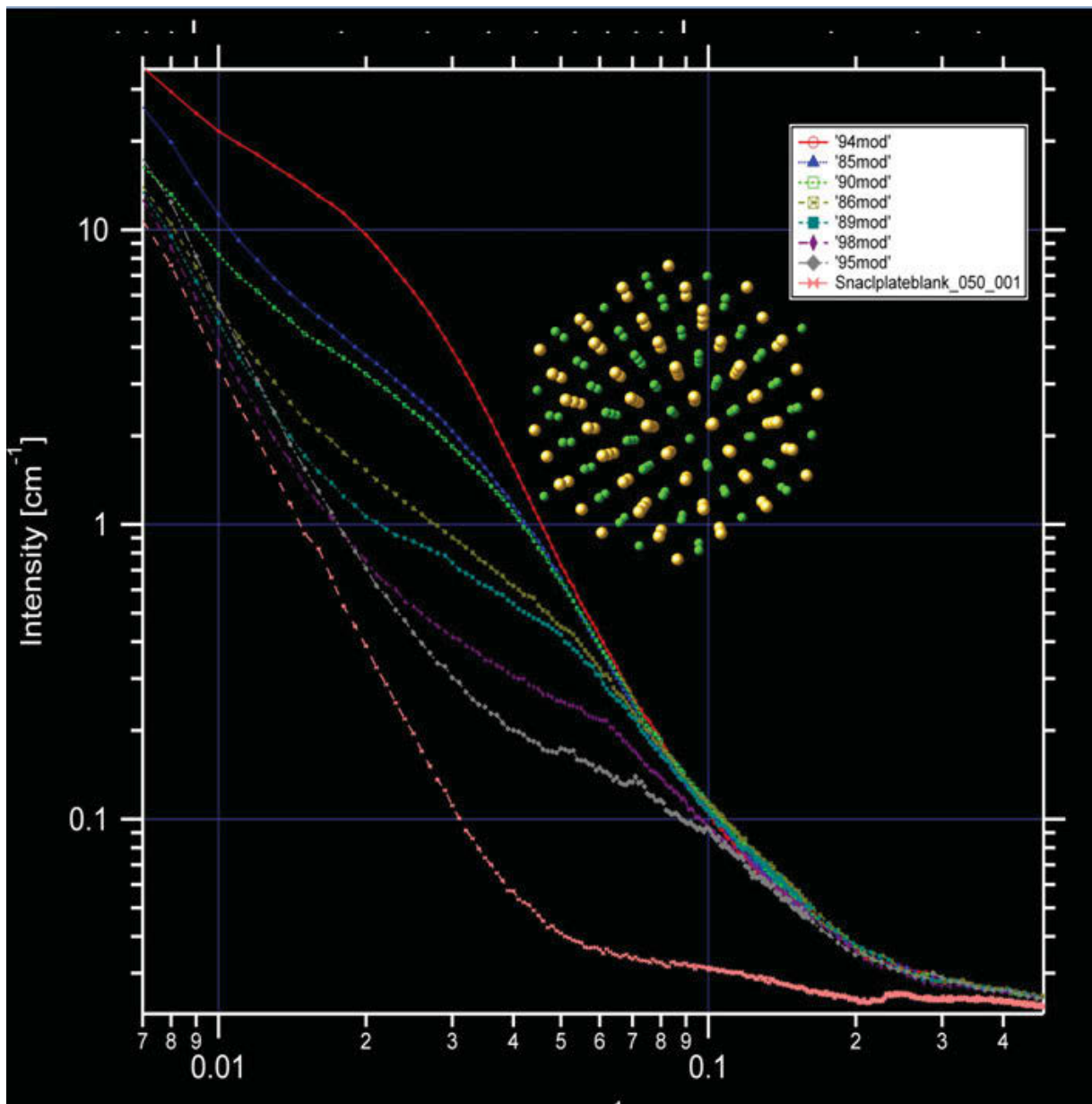


Figure 17 Bessel Function w/ Lg QD representation

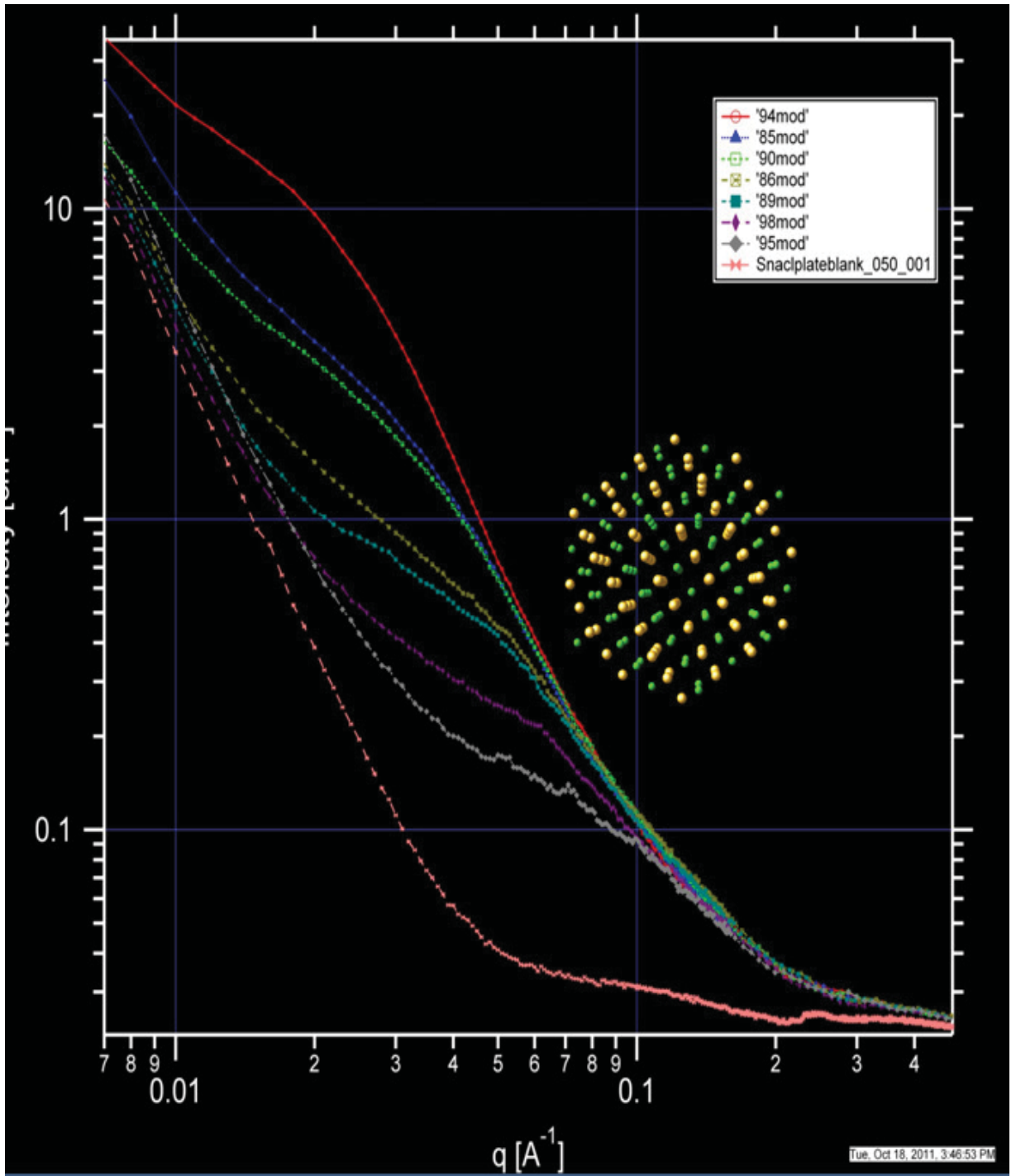


Figure 18 Bessel Function w/ Med QD representiaon

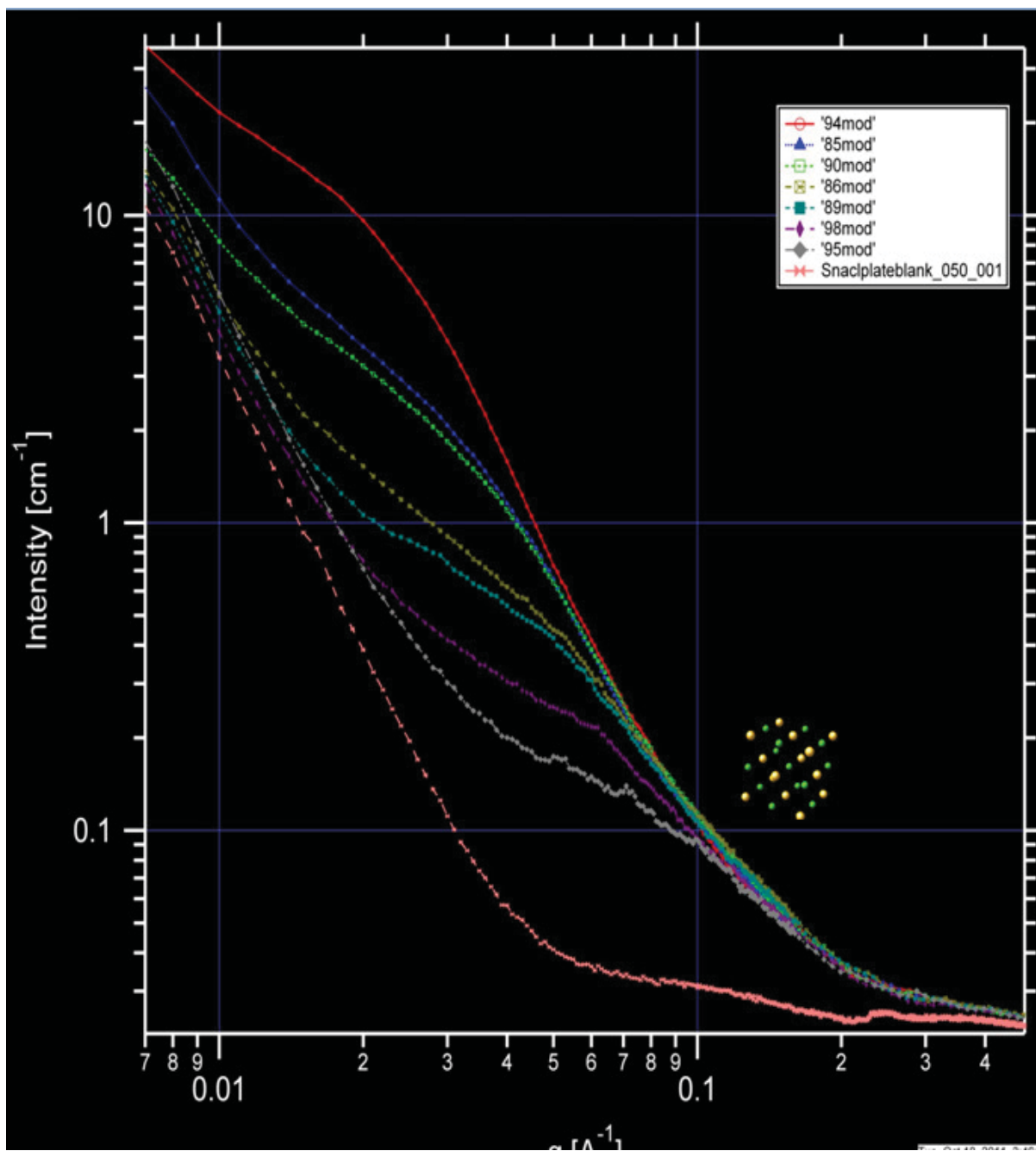


Figure 19 Bessel function w/sm QD representation

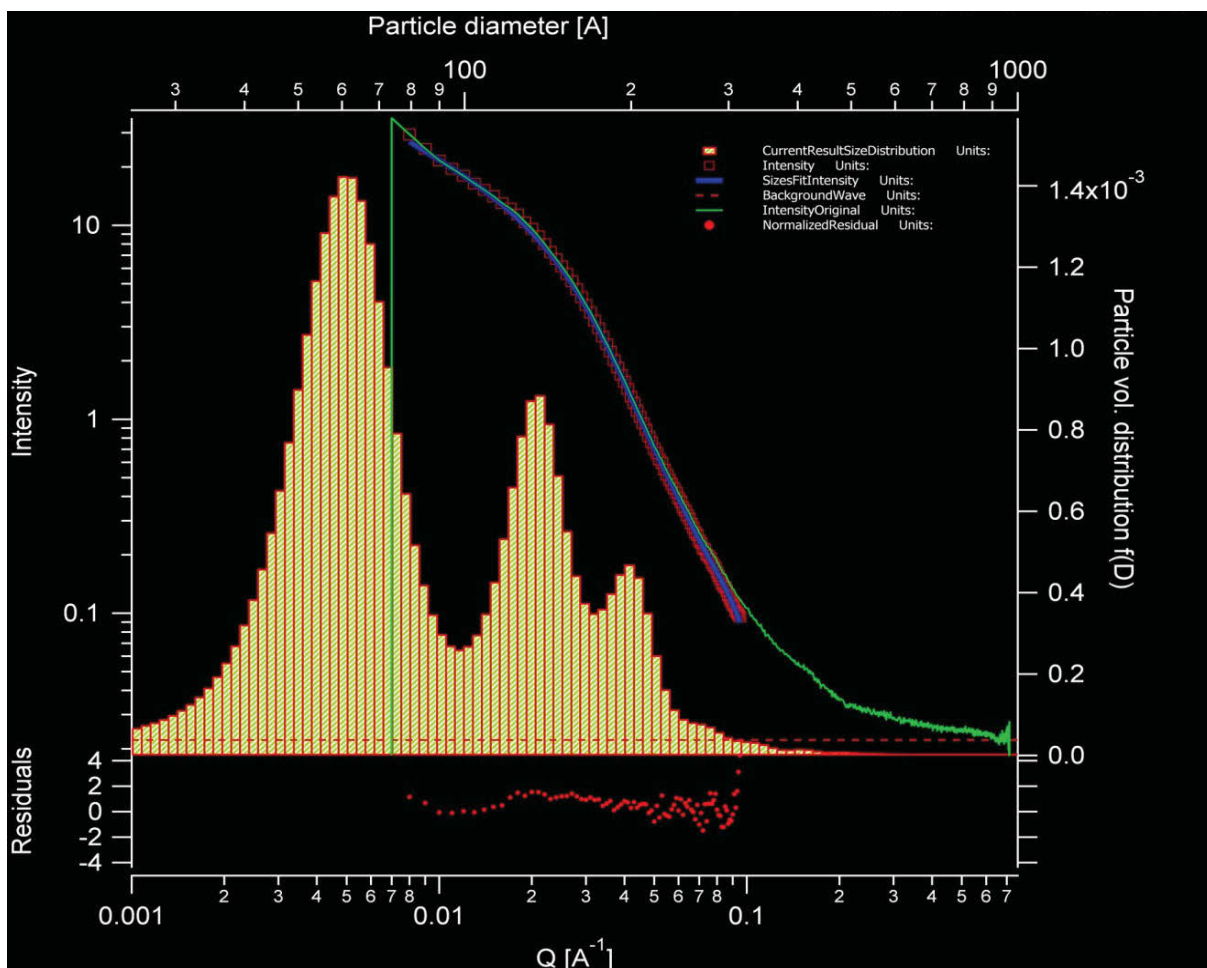


Figure 20 Size and Volume Distribution Plot

Figure 20 shows a size and volume distribution analysis of the upper-leftmost Bessel function. As one can see the quantum dots in this region are predominantly 6 nanometers in diameter with a significant population as well around 15 and 20 nanometers. Using IGOR PRO for analysis of the SAXS data, we focused our work on the largest peak. In Figure 21, a more in depth calculation of the size and volume distribution of the upper-most Bessel function is 6 nanometers.

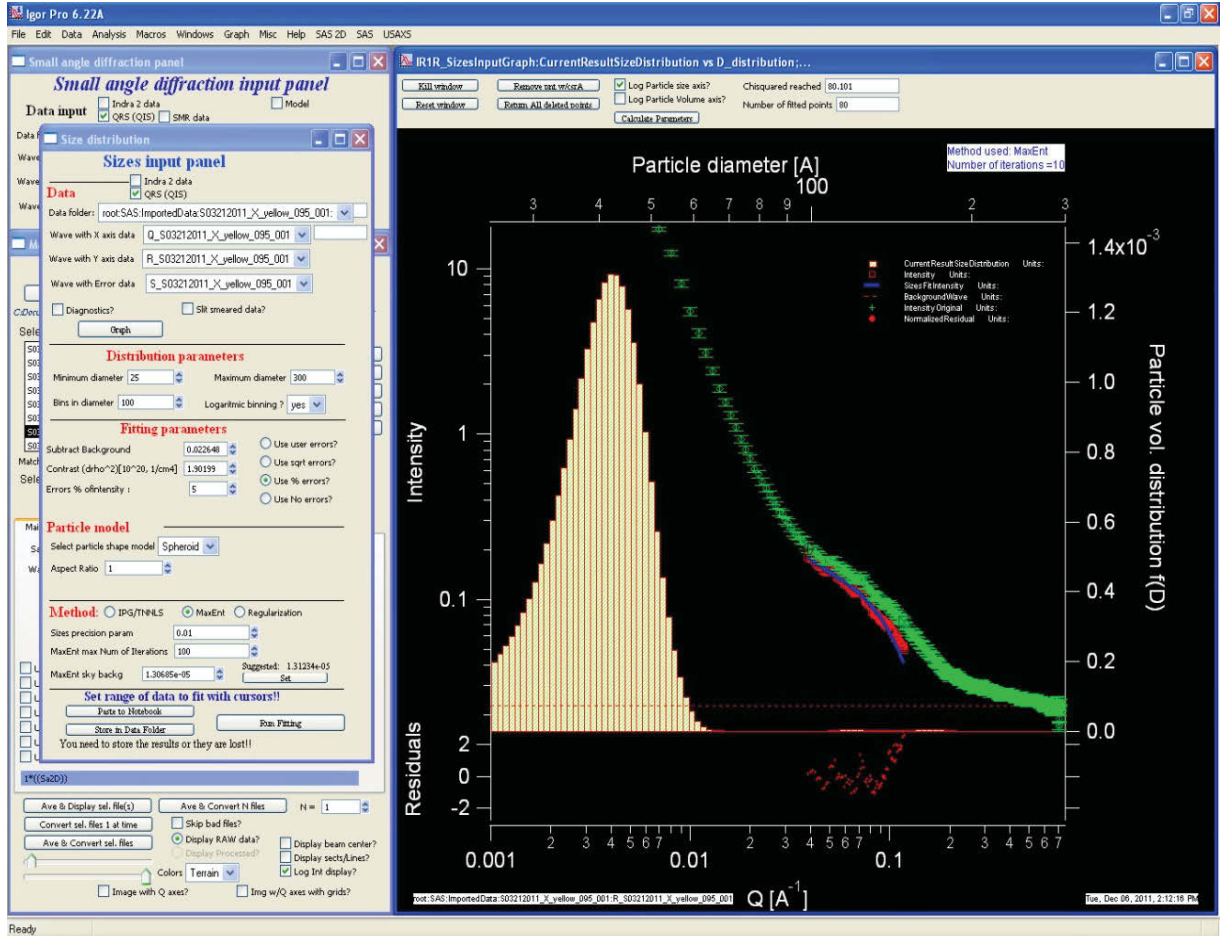


Figure 21 Size and Volume Distribution

Combined with the previous slides, this is the first definitive SAXS data we have collected and is absolute empirical proof that we have succeeded in producing CuCl Quantum Dots in a NaCl matrix.

TEM/EDS

Preliminary TEM data obtained at Youngstown State University from a JEOL 2100 with LaB₆ source at 200 kV showed sample degradation, as seen in Figures 22-26. We believed that a lower voltage TEM with a cryogenic sample holder would help eliminate this problem and provide enough magnification to directly measure nanoparticles sizes. Use of the JEOL 1400 TEM w/ Gatan Cryoholder at the Center for Functional Nanomaterials at Brookhaven National Laboratory would provide us the capability to directly measure nanoparticle sizes, obtain crystal morphology and establish TEM as a characterization method for challenging materials like these CuCl quantum dots embedded in a NaCl matrix.

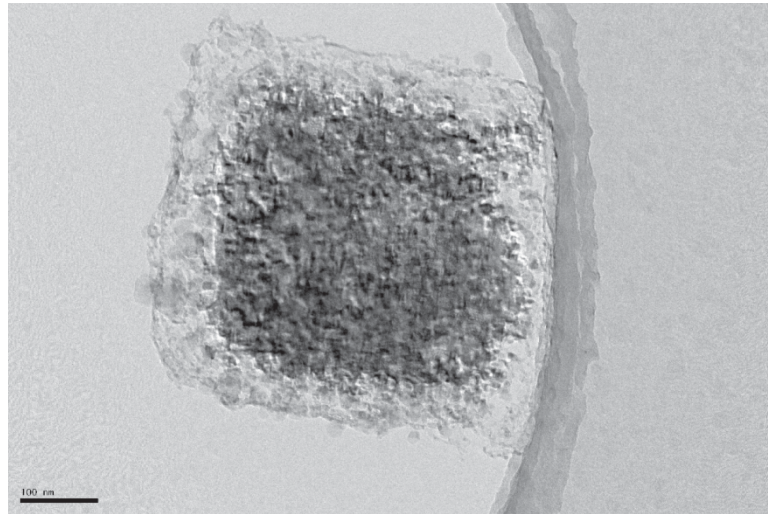


Figure 22- 200kV / 100nm at ~30 sec.

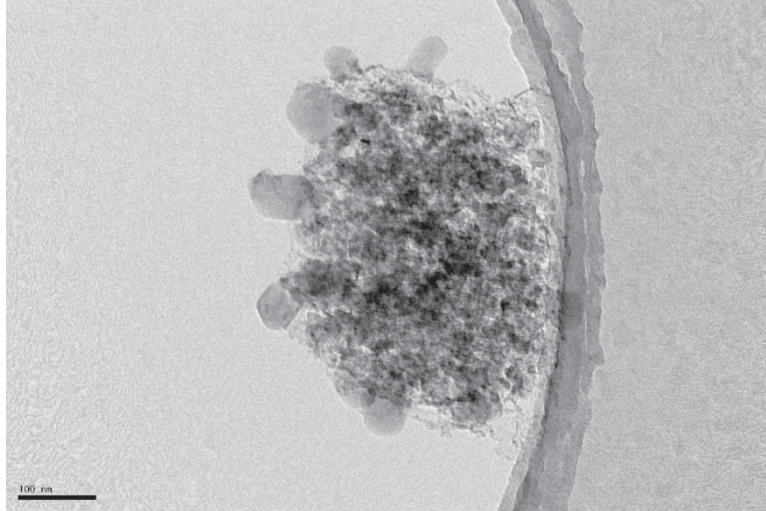


Figure 23- 200kV / 100nm at T=3 min.

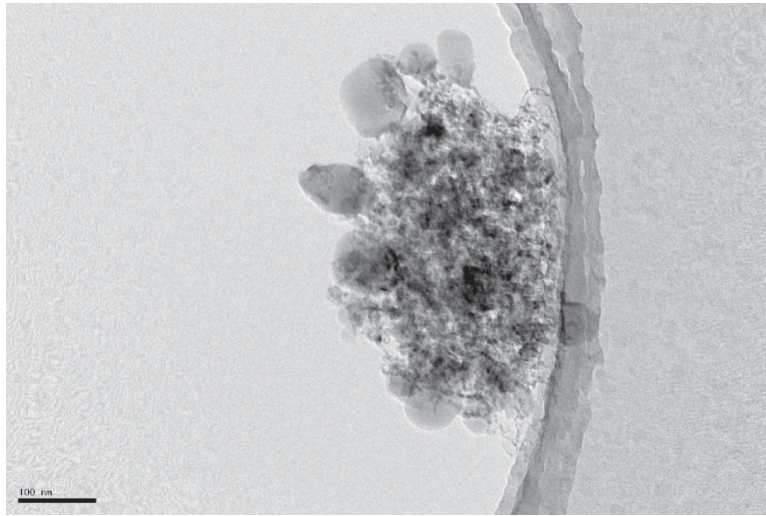


Figure 24 - 200kV / 100nm at T=5 min.

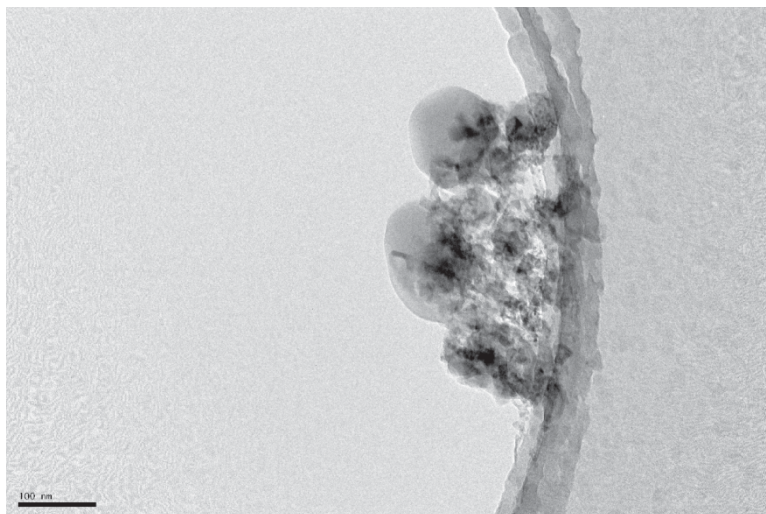


Figure 25- 200kV / 100nm at T=9 min.

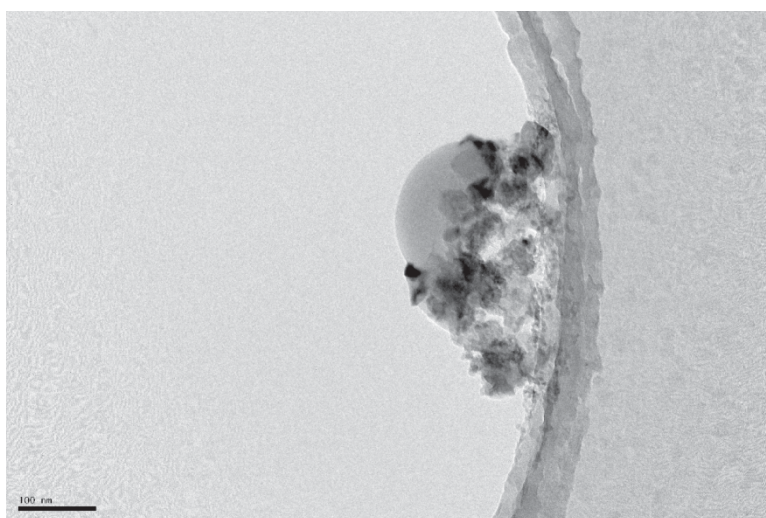


Figure 26- 200kV / 100nm at T=10 min.

Therefore the transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) portions of this work were performed at the Center for Functional Nanomaterials at Brookhaven National Laboratory. The electron micrograph illustrated in Figure 27 was collected on a JEOL JEM-1400 Low Voltage TEM operated at 120 kV

with smallest possible objective and condenser apertures, spot size 3 and captured using a Gatan 2048 x 2048 pixel CCD camera coupled to Gatan Digital Micrograph software for archival and analysis. Selected representative samples were cleaved and ground to sub-micron size in a purpose-built automated agate ball mill with agate grinding media. Ground samples were immersed in hexanes and sonicated for approximately twenty minutes in a scintillation vial prior to introduction to the TEM grid. The TEM grids used were Ted Pella Lacey Carbon, 200 mesh, Nickel substrate. Sample introduction was achieved by dipping the TEM grid in the settled hexanes solution and secured with drying by heat lamp. TEM grids were mounted in a Gatan Cryoholder which had been processed for use on a Gatan 655 Turbo Pumping Station and equipped with a Gatan Model 900 Smart Set temperature controller. Once introduced to the TEM, column samples were cooled and maintained at 77 K for the duration of the imaging cycle to reduce beam damage. Here there is unmistakable evidence of nanoparticles sizes under 20 nanometers. Each one of the dark spots are CuCl quantum dots of varying sizes and indicates a spherical morphology.

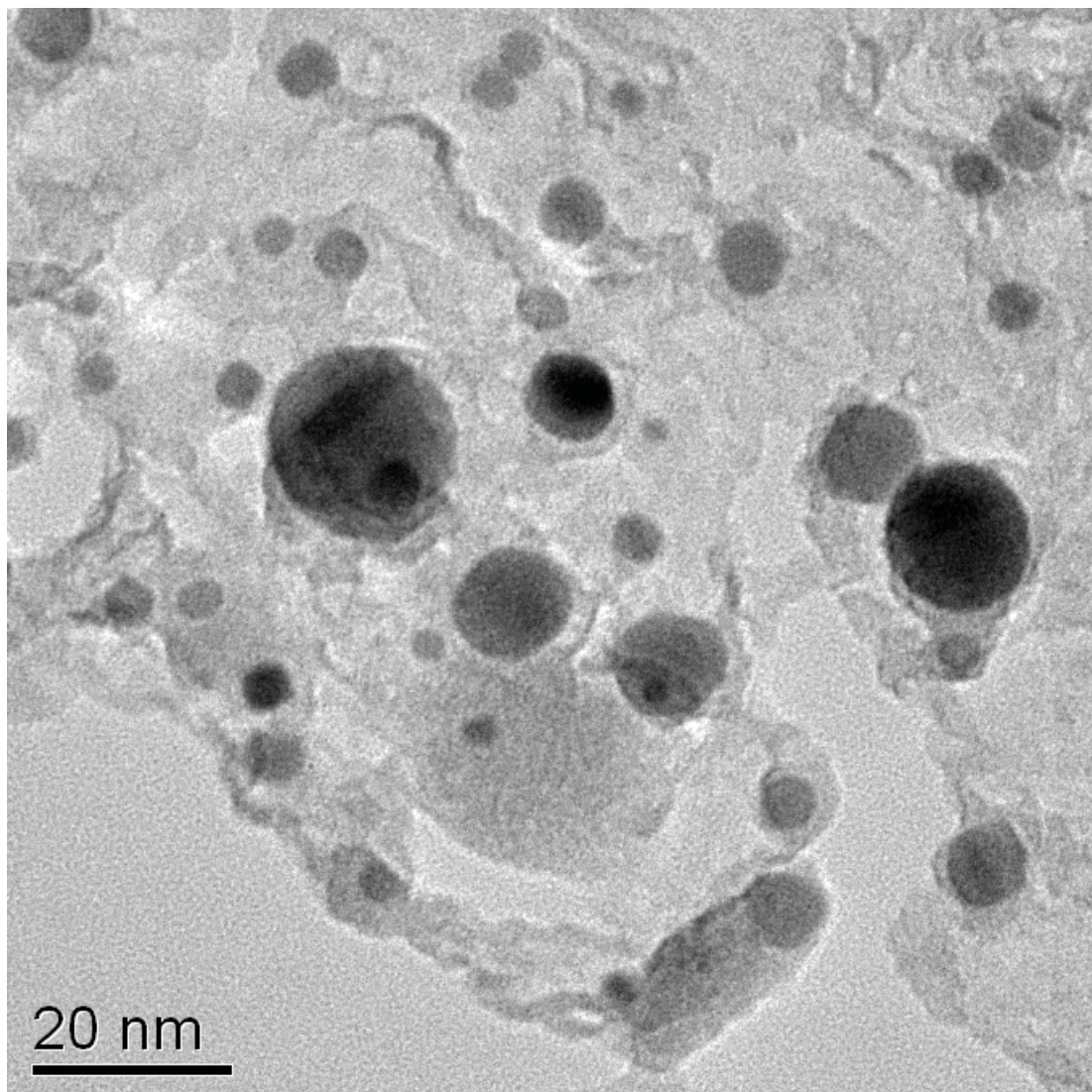


Figure 27 TEM micrograph

The EDS spectrum illustrated in Figure 28 was collected using a JEOL JEM-2100F HRTEM equipped with an Oxford Energy TEM 250 EDS operated in single spectrum mode with probe size 2 nm. EDS data was analyzed using the INCA Microanalysis System. The data collected from a single nanoparticle indicate an approximate 1:1 ratio of copper to chlorine and suggest CuCl as the empirical formula. Further confirming we produced CuCl quantum dots.

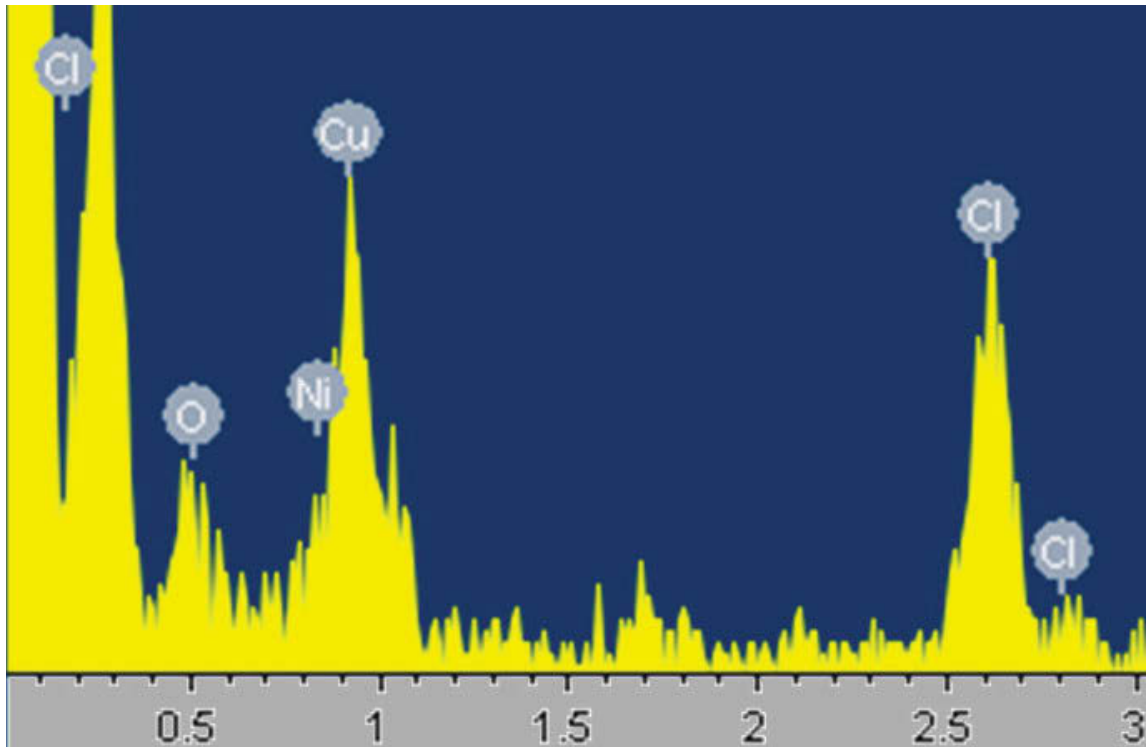


Figure 28 EDS peaks

Applications

Scientists and engineers are making breakthrough discoveries every day. These scientists are building devices that get smaller and smaller. Many things today are powered by transistors and these devices are not without exception to the “if we build it smaller it will be better” concept. Microscopic electronic switches that perform data logic can perform millions of operations in fractions of a second. Quantum dots have shown that they can act as single-electron transistors and show the Coulomb blockade effect in electronic applications (Reed 1993). Scientists and researchers are working to increase the speed of these microchips and every eighteen months the speed doubles (Moore 1965). Therefore incorporating quantum dots into these types of applications would be beneficial. For

instance, larger quantum dots have a greater spectrum-shift towards red compared to smaller dots, and exhibit less pronounced quantum properties. Conversely, the smaller particles allow one to take advantage of more subtle quantum effects. Researchers at Los Alamos National Laboratory have developed a wireless device that efficiently produces visible light, through energy transfer from thin layers of quantum wells to crystals above the layers (Bastard, Mendez, Chang and Esaki 1982).

Computing

Solid state quantum computation is one of the most hopeful technologies for the employment of quantum dots. By applying small voltages to the leads, the flow of electrons through the quantum dot can be controlled and thereby precise measurements of the spin and other properties therein can be made. With several entangled quantum dots, or qubits, plus a way of performing operations, quantum calculations and the computers that would perform them might be possible (Miller 1984).

Solar Cells

A principle element of third generation solar cells is the quantum dot. A quantum dot is a nanometer-sized semiconductor whose photon generated charge carriers known as excitons are confined in all three spatial dimensions (Rhodes, Asakura, Brenner, Hansch Kamiya, Krausz, Monemar, Venghaus, Weber and Weinfurter 2005). As a result of this confinement the material exhibits electronic properties somewhere in between those of the bulk and those of discrete molecules. Quantum dots were discovered in the 1980s by

multiple researchers including Bawendi, Brus and others. The confinement of excitons within the nanocrystals is responsible for the altered electronic properties of quantum dots. The smaller the size of the crystal the larger the band gap becomes. The property most desirable in quantum dots in the current context is the ability to tune the band gap of the dot to match a particular need. A distinct advantage of quantum dots is that multiple band gaps can be produced from the exact same material by producing different size crystals. However, like many third generation solar cells, the materials used to produce quantum dots are frequently toxic. Research is underway to discover non-toxic materials useful as quantum dots

Biology

Organic dyes are used for a vast range of biological analysis, but with continued research the many of these dyes are unable to keep up with the flexibility that is being required of these dyes. Quantum dots have a place in filling that void where organic dyes cannot be used. One of the glaring attributes of QDs is how vibrant the light is that is emitted from QDs. This is due to the high extinction co-efficient combined with a comparable quantum yield to fluorescent dyes as well as their stability allowing much less photobleaching. (Ballou, Lagerholm, Ernst, Bruchez and Waggoner 2004) Quantum dots are typically 20 times brighter and 100 times more stable than traditional fluorescent tags (Ballou, Lagerholm, Ernst, Bruchez and Waggoner 2004).

Quantum dots are becoming a very versatile commodity in sensitive cellular imaging.

These advances in quantum chemistry such as photostability of quantum dots has allowed

advances and allows the acquisition of many consecutive focal-plane images that can be reconstructed into a high-resolution three-dimensional image (Walling, Novak and Shepard 2009).

Other advances in the photostability of quantum dot probes is the real-time tracking of molecules and cells over extended periods of time. Quantum dots can be used to tag specific antibodies, peptides, nucleic acid, or small-molecule ligands. Research has already been done in which QDs are being observed in lymph nodes of laboratory animals (Ballou, Lagerholm, Ernst, Bruchez and Waggoner 2004). Cancer research may in fact be advanced due to the ability to image single-cell migration in real time.

Experimental research has been working on improving existing methods for delivering a gene-silencing tool, known as siRNA, into cells (Howarth, Liu, Puthenveetil, Zheng, Marshall, Schmidt, Wittrup, Bawebdi and Ting Nat 2008)

Toxicity is a very concerning issue that over shadows quantum dots for the use in biological systems. CdSe nanocrystals are highly toxic to cultured cells under UV illumination (Pelley, Daar and Saner 2009). A huge stumbling block is photolysis. This is when UV dissolves some of the semiconductor particles within the QD and toxic cadmium ions are released (Pelley, Daar and Saner 2009).

LED

Quantum dots are semiconductors with tunable bandgaps and are becoming more and more sought after for the production of light emitting devices. Investigations are taking place to use quantum dots as light-emitting diodes to make displays and other light

sources, such as QD-LED displays, and QD-WLED (Chapman 1970). In June, 2006, QD Vision announced technical success in making a proof-of-concept quantum dot display and shows a bright emission in the visible and near infra-red region of the spectrum (Chapman 1970). The light emitted by quantum dots are in a Gaussian distribution and are desired in making displays and the electrical energy is not converted into as much heat and therefore a truer color spectrum is observed. It is possible with combinations of quantum dots that white light can be produced. A color liquid crystal display (LCD), for example, is usually powered by a single fluorescent lamp that is color filtered to produce red, green, and blue pixels. Displays that intrinsically produce monochromatic light can be more efficient, since more of the light produced reaches the eye (Chapman 1970).

Conclusion

The applied research question which began this work focused on the possibility of replacing complicated, expensive and highly toxic semiconductor quantum dots with a simple, non-toxic equivalent. The empirical evidence suggests this possibility exists. The photoluminescence spectrum collected from the representative sample indicates a strong peak near 388 nm, a telltale sign of the Z_3 exciton known in copper chloride bulk material. The SAXS analysis of the same sample indicates order consistent with spherical nanocrystals of particular sizes distributed throughout the sample volume. The TEM micrograph of the same representative sample indicates spherical morphology of nanoparticles in the same size regimes and relative abundances indicated by the SAXS analysis. The EDS spectrum collected on a single nanocrystal isolated from the same

sample indicates a composition of 1:1 copper to chlorine. Based on the Z_3 observation, the SAXS data that confirming nanocrystals within the NaCl matrix and our TEM/EDS data we are inclined to conclude that the bulk sodium chloride crystal contains non-toxic, easily synthesized nanocrystalline copper chloride quantum dots which mimic their highly-toxic and sophisticated counterparts.

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