Efficient Integration of Plasmonic and Excitonic Properties of Metal and Semiconductor Nanostructures via Sol-Gel Assembly

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Efficient Integration of Plasmonic and Excitonic Properties of Metal and Semiconductor Nanostructures via Sol-Gel Assembly

A thesis submitted in partial fulfillment of the requirements for the Degree of Master of Science at Virginia Commonwealth University by Dilhara Liyanage

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ACKNOWLEDGEMENT

I sincerely thank my loving husband, Dhanushka Liyanage, my parents, Rev. Athula and Mrs. Prabha Rebecca Dewasinghe, my two brothers and their families, Ashan & Menaka, Ranil & Piumi and their daughter Amanda, my dearest sister Shihara and my grandparents, Victor and Glory Manuel for their love and support. I am truly blessed to have a wonderful family and words cannot explain their love, encouragement and advise. I wouldn’t be where I am today without them! I must thank my parents for all the sacrifices they have made in their life for me to accomplish in education. Knowing that they would provide me with everything I needed for my studies was a huge support and helped me focus on my educational goals. I’m so very grateful for their love, prayers, blessings, financial support and for encouraging me in every way during hard times in college. I’m so thankful to my loving husband, Dhanushka for his love. A master’s degree in Chemistry from VCU would only be a dream in my life without his financial support and also his constant encouragement, understanding, loving me for who I am and most importantly, his sense of humor and smile that kept me thriving in life.

It has been a great privilege to be a student of Dr. Indika Arachchige. I am very grateful to him for giving me the opportunity to join his lab and taking his valuable time to teach and guide me in research. I would not be able to achieve this goal in education within a year without his advice, enormous support and encouragement. I’m forever thankful for everything that he has done to help me since the day I walked into his office.

I would like to thank Dr. Ümit Özgür and Tanner Nakaragawa from VCU Electrical Engineering for helping us with TRPL studies.
I would like to thank Dr. Christopher Ehrhardt and Terrie Simmons-Ehrhardt for their advice, encouragement and support throughout past few years. I would not be reaching this goal without their help! I’m so thankful to them for taking time out of their busy schedules to help me and I must specially thank for the wonderful research experience in forensic chemistry which I will never forget.

I would like to extend my gratitude to Dr. Julio Alvarez for his guidance in graduate school. I can’t imagine completing my masters without his help and advice. I’m thankful to Dr. Hani El-Kaderi for his advice and support as a faculty member of my thesis committee.

I would like to thank Dr. Sally Hunnicutt, Dr. Joseph Topich and Mrs. Ruth Topich for their support, encouragement and for the opportunity to teach under their mentorship.

I would also like to thank all my friends in the Arachchige research lab for helping me in many ways. It has been a great year working with you all!

I’m thankful to Virginia Commonwealth University Department of Chemistry for giving me the opportunity to excel in research.

Finally, I would like to thank others, whom I have not listed above, but have helped me in many ways during this journey at VCU.

“The works of the Lord are great, studied by all who have pleasure in them.”

Psalm 111:2
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................ vii - xi

LIST OF TABLES .......................................................................................................... xii

LIST OF SCHEMES ..................................................................................................... xiii

ABSTRACT ..................................................................................................................... xiv - xvi

CHAPTER 1. Introduction ............................................................................................. 1 - 22

1.1. Nanomaterials
1.2. Semiconductors
1.3. Quantum Confinement and Optical Properties of Nanomaterials
1.4. Synthesis of Nanoparticles
1.5. Metal Nanoparticles and Surface Plasmon Resonance
1.6. Metal – Semiconductor Hybrids
1.7. Sol-Gel Method and Aerogels
1.8. Nanoparticle Condensation Strategy
1.9. Thesis Statement

CHAPTER 2. Experimental Methods and Materials Characterization

Techniques .................................................................................................................... 23 - 52

2.1 Materials
2.2 Experimental Techniques
    2.2.1 Schlenk Line Techniques.
2.2.2 Inert Atmosphere - Glove Box

2.2.3 Supercritical CO₂ Drying

2.3 Synthesis of Surface Functionalized CdSe Nanostructures

2.3.1 Synthesis of CdSe Nanorods.

2.3.2 Synthesis of CdSe Nanocrystals.

2.3.3 Surface Functionalization of CdSe with Thiolate Ligands

2.4 Synthesis of Glutathione Functionalized Ag Hollow Particles

2.5 Synthesis of Metal-Semiconductor Hybrid Hydrogels and Aerogels.

2.6 Materials Characterization Techniques

2.6.1 UV-Visible Spectroscopy

2.6.2 Solid State Diffuse Reflectance UV-Visible Spectroscopy

2.6.3 Photoluminescence Spectroscopy

2.6.4 Time-Resolved Photoluminescence Spectroscopy

2.6.5 Transmission Electron Microscopy

2.6.6 Powder X-ray Diffraction

2.6.7 X-ray Photoemission Spectroscopy

2.6.8 Inductively Coupled Plasma Optical Emission Spectrometry

2.6.9 Surface Area and Porosimetry Analysis

CHAPTER 3. Results and Discussion ..........................................................53 - 82

CONCLUSIONS .........................................................................................83 - 85

REFERENCES ..........................................................................................86 - 97

VITA ...........................................................................................................98 - 100
LIST OF FIGURES

Figure 1.1. Size range of the nanomaterials and comparative sizes of biological entities, living organisms, and macroscopic materials.................................................................2

Figure 1.2. An energy level diagram of bulk metals, semiconductors, and insulators.................................................................6

Figure 1.3. Schematic diagram of a semiconductor demonstrating the generation of electron-hole pair (i.e. exciton) via photoexcitation process. .........................................................6

Figure 1.4. Size dependent electronic energy levels of semiconductors, from continuous bands in bulk to discreet molecular orbitals.................................................................8

Figure 1.5. Geometries of nanoscale materials along with bulk crystalline solids (3-D), quantum well (2-D), quantum wire (1-D), and a quantum dot (0-D) ..............................................9

Figure 1.6. A schematic illustration of the surface plasmon resonance of metal NPs.................................................................10

Figure 1.7. Schematic of laser ablation technique of NP synthesis in top-down method.................................................................14

Figure 1.8. La Mer style nucleation and growth mechanism in colloidal synthesis.................................................................15
Figure 1.9. Representation of sol-gel condensation of nanoparticles into aerogel and xerogel..............................................................19

Figure 2.1. Schlenk line apparatus used in the air-free synthesis of semiconductor NPs..............................................................25

Figure 2.2. Phase diagram of CO$_2$..........................................................27

Figure 2.3. A schematic description of a double beam UV-Vis spectrometer..............................................................32

Figure 2.4. A schematic representation of the absorption and emission of light by phospholuminescence processes fluorescence and phosphorescence..............................................................35

Figure 2.5. Different events of incident electron beam after interacting with the sample..............................................................37

Figure 2.6. Schematic diagram of a standard X-ray tube..........................39

Figure 2.7. Illustration of electronic transitions between shells for X-ray radiation..............................................................40

Figure 2.8. Diffraction of X-rays from crystal planes..........................41

Figure 2.9. Diagram of the X-ray photoelectron spectrometer and the hemispherical detector..............................................................44

Figure 2.10. Adsorption (black)/desorption (blue) isotherm of a porous solid displaying the areas of the adsorption and desorption, micropore filling (I), monolayer formed (II), multilayer adsorption (III), pore filling (IV), and capillary condensation (V)..........................49
Figure 2.11 Six types of adsorption isotherms……………………………………..50

Figure 2.12 Four types of hysteresis loops………………………………………….51

Figure 3.1. UV-Vis absorption spectra of CdSe NPs(a) and CdSe NRs(b) demonstrating the first and second excitonic transitions (red) and photoluminescence spectra demonstrating band edge emission (blue)……………………………………………………………………………………………………57

Figure 3.2. The normalized UV-Vis absorption spectra of CdSe NPs (red) and Ag hollows (green) demonstrating the overlap of the first excitonic absorption of CdSe NPs with the plasmonic resonance of Ag hollow NPs [a], CdSe NRs (red) and Ag hollows (green) demonstrating the overlap of the second excitonic absorption of CdSe NRs with the plasmonic resonance of Ag hollow NPs [b]……………………………57

Figure 3.3. TEM images of the (A) CdSe NPs, (B) CdSe NRs, and Ag hollow NPs with LSPR at (C) 500 nm, (D) 515nm used in the synthesis of CdSe/Ag hybrids……………………………………………………………………………………61

Figure 3.4. Photographs of CdSe nanorods/Ag hydrogels [A] with varying Ag content: (a) 0, (b) 0.2%, (c) 0.5%, (d) 0.7%, and (e) 1%, CdSe nanoparticles/Ag hydrogels [B] with varying Ag content: (f) 0, (g) 0.2%, (h) 0.5%, (i) 0.7%, and (j) 1%. The elemental compositions were calculated according to the amount of precursor used in the synthesis assuming a 100% yield…………………………………………………………62

Figure 3.5. Photographs of CdSe nanorods/Ag hydrogels with varying Ag content: (a) 0, (b) 0.2%, (c) 0.5%, (d) 0.7%, and (e) 1% under
UV light. The elemental compositions were calculated according to the amount of precursor used in the synthesis assuming a 100% yield.

**Figure 3.6.** Photographs of selected CdSe/Ag aerogel monoliths with 1% Ag loading. Top view [A] and side view [B]. Scale bar is in centimeters.

**Figure 3.7.** Low resolution TEM images of (A) spherical shaped CdSe/Ag aerogel and (B) rod shaped CdSe/Ag aerogel. Dark contrast areas show the 3-D nature of the materials.

**Figure 3.8.** Representative nitrogen adsorption/desorption isotherm (blue) of spherical shaped CdSe and corresponding BJH pore size distribution (red) [A], and isotherm (blue) of spherical shaped CdSe with 0.5% Ag loading and pore size distribution (red) [B].

**Figure 3.9.** Representative nitrogen adsorption/desorption isotherm (blue) of rod shaped CdSe and corresponding BJH pore size distribution (red) [A], and isotherm (blue) of rod shaped CdSe with 0.5% Ag loading and pore size distribution (red) [B].

**Figure 3.10.** PXRD Pattern of CdSe NP (A) and NR (B) aerogel (red), ICDD-PDF overlays of hexagonal CdSe (PDF # 08-0459, black) and Ag hollow aerogel (blue), cubic Ag (PDF # 01-0870-719, gray) are shown as vertical black lines.

**Figure 3.11.** XPS spectra of CdSe semiconductor aerogel (A) Cd (3d5/2), (B) Se (3d5/2), and (C) Ag (3d5/2).
**Figure 3.12.** XPS spectra of CdSe/Ag metal-semiconductor aerogel (A) Cd (3d\(\frac{5}{2}\)), (B) Se (3d\(\frac{5}{2}\)), and (C) Ag (3d\(\frac{5}{2}\))...........................................73

**Figure 3.13.** Solid-state absorption spectra of CdSe NPs gels demonstrating the bandgap changes of the aerogels with increasing nominal Ag content 0 – 1%..................................................................................................77

**Figure 3.14.** Solid-state PL emission spectra of spherical shaped CdSe and CdSe/Ag hybrid aerogels with 0, 0.2%, 0.5%, 0.7%, and 1% Ag loading at 77 K..........................................................77

**Figure 3.15.** Solid-state absorption spectra of CdSe NRs demonstrating a red shift, quenching of bandgap and tailing effects with increasing Ag composition in the aerogels.................................................................79

**Figure 3.16.** Solid-state PL emission spectra of rod shaped CdSe and CdSe/Ag hybrid aerogels with low to high (0 - 10%) Ag loading At 77 K........................................................................................................80
LIST OF TABLES

Table 3.1. The densities of CdSe nanorods/Ag aerogels with varying Ag content: (a) 0, (b) 0.2%, (c) 0.5%, (d) 0.7%, and (e) 1%. The elemental compositions were calculated according to the amount of precursor used in the synthesis assuming a 100% yield……………………………………………………………………..64

Table 3.2. The volumes and nominal moles of CdSe, and Ag hollow particle sols used in the synthesis of CdSe/Ag aerogels along with the experimental molar ratio of CdS:Ag obtained from ICP-OES……………………………………………………………………..74

Table 3.3. The decay time and amplitude rations from biexponential fits for all emission peaks of CdSe/Ag aerogels with different Ag loading……………………………………………………………………………..82
LIST OF SCHEMES

**Scheme 3.1.** Synthesis of MUA capped CdSe NRs and NPs..........................55

**Scheme 3.2.** Representation of oxidation-induced direct cross linking of thiolate functionalized CdSe and Ag NPs to produce NP network of CdSe/Ag hybrids.................................................................60
ABSTRACT

Efficient Integration of Plasmonic and Excitonic Properties of Metal and Semiconductor Nanostructures via Sol-Gel Assembly

A thesis submitted in partial fulfillment of the requirements for the Degree of Master of Science at Virginia Commonwealth University by

Dilhara Liyanage

Advisor: Dr. Indika U. Arachchige

Department of Chemistry

Research in nanoscience has gained noteworthy interest over the past three decades. As novel chemical and physical properties that are vastly different from extended solids are realized in nanosized materials, nanotechnology has become the center of attention for material in research community. Much to our amazement, investigations in the past two decades revealed that the nanocrystalline semiconductors are “THE PRIME CANDIDATES” to meet the growing energy demand, sensor development, cellular imaging and a number of other optoelectronic applications. Nonetheless, synthesis of
nanostructures with control over physical parameters is not sufficient, yet assembling
them into functional nanoarchitectures with unique and tunable physical properties is
critical for device integration studies. Among bottom-up assembling methods, sol-gel
method has received noteworthy interest to produce macroscopic nanostructures of metal
and semiconductor NPs with no use of intervening ligands or supports.

In 2005, condensation of pre-formed semiconductor NPs (CdSe, CdS, ZnS and PbS)
into voluminous gels is reported via controlled destabilization of the surfactant ligands.
The resultant chalcogenide aerogels are reported to exhibit extremely low density, high
surface area and porosity, and quantum confined optical properties of the NP building
blocks. More recently, this method has been extended for the assembly of metal NPs,
where transparent and opaque nanostructures (aerogels) of Ag and Au/Ag NPs were
produced. The aerogels produced by condensation of NPs are low dimensional (fractal)
nanostructures and exhibit a physically connected network of colloidal NPs. Interactions
between NPs in a gel structure are intermediate of those of the ligand stabilized NPs and
core/shell hetero-nanostructures (e.g. Au@CdSe NPs) with the potential to couple
chemically dissimilar systems. In this research study, NP condensation strategy has been
utilized to efficiently integrate the plasmonic and excitonic properties of metal and
semiconductor nanostructures to produce high-efficiency hybrids that exhibit unique
tunable physical and photophysical properties.

Two hybrid systems composed of spherical CdSe/Ag hollow NPs and rod shaped
CdSe/Ag hollow NPs were investigated for the fabrication of metal-semiconductor hybrid
aerogels. The first excitonic energy of spherical CdSe NPs is overlapped with the
plasmonic energy of Ag hollow NPs at 515 - 530 nm. The second excitonic energy of rod
shaped CdSe is overlapped with the plasmonic energy of Ag hollow NPs at 490 - 505 nm. The photophysical properties of both systems were thoroughly probed through UV-Visible absorption, photoluminescence (PL), and time-resolved (TR) PL spectroscopy. A novel hybrid emission emerged at 640 nm (for spherical CdSe/Ag hollow NPs) and 720 nm (for rod shaped CdSe/Ag hollow NPs) with ~0.2-1% Ag loading. TRPL studies revealed 685 ns and 689 ns PL decay times for hybrid emissions, which are vastly different from the band-edge and trap state emission of phase pure spherical and rod shaped CdSe aerogels respectively, supporting the generation of novel radiative decay pathways. Overall, synthesis of CdSe/Ag hybrid aerogels with novel/tunable photophysical properties will add to the toolbox of semiconductor aerogels with the potential application in future light harvesting technologies.
CHAPTER 1

INTRODUCTION

Research in nanoscience and nanotechnology has been one of the most resounding topics in the past few decades amongst scientists. Greater attention has been drawn into nanoscience because of its ability to generate novel/tunable physical properties that do not exist in bulk solid materials. For instance, unique optical, electronic, magnetic, and catalytic properties have been achieved as the size is decreased from bulk to nanomaterial, more specifically, when the material size is in the range of 1 – 100 nm. This can potentially lead to advances in applications in optoelectronic and energy conversion devices, optical detectors and sensors as well as photo-/electro-catalysts. As new devices are being developed, making them in miniature size became an important endeavor due to the high demand of handheld electronic devices. This has been made possible with nanosized semiconductors, transistors, and sensors. Therefore, greater attention is given to the development of techniques and procedures for synthesis of nanoscale materials. The use of nanoparticles (NPs) were limited due to the lack of proper assembling methods and recently there were many reports on efficient assembly of nanoparticles with passivated surfaces. Ligand coated NPs provides a great platform to tune the interfacial properties when assembled into hetero-nanostructures. Further, these methods provided the ability to assemble chemically similar and dissimilar components into single hybrid nanostructures. An introduction to nanomaterials, semiconductors, plasmonic metals, and their unique physical properties as well as hybrid materials composed of metal and semiconductors will be discussed in this chapter. Further, the importance of sol-gel chemistry in the assembly of metal and semiconductor NPs into individual or
hybrid superstructures will also be discussed with an aim of developing novel, efficient nanomaterials for energy harvesting technologies.

1.1. Nanomaterials

A nanometer (nm) can be depicted as one billionth of a meter (m) or one millionth of a millimeter (mm) and roughly equal to the length of ten hydrogen atoms in a row.\textsuperscript{5} Materials approximately between 1 – 100 nm at least in one dimension are identified as nanoscale materials. When the material size is reduced to nanoscale, the surface-to-volume ratio of the materials increases allowing higher performance and significantly different optical, electrical, physical, magnetic, and mechanical properties compared to its bulk material. These remarkable properties were observed in the nanoscale while the composition of the material is equivalent to that of the bulk material.\textsuperscript{5}

Even though the interest and attention towards nanomaterials were given in the past few decades, the use of nanomaterials have been around for centuries. In 1857, Michael Faraday reported the colloidal synthesis of gold particles and his report is recognized as the first scientific report in nanoscience.\textsuperscript{6} Since then, many reports have been published in scientific journals even before the age of nanoscience and nanotechnology began.

![Image of sizes comparison](image)

**Figure 1.1.** Size range of the nanomaterials and comparative sizes of biological entities, living organisms, and macroscopic materials.
Nowadays, the area of nanoscience is driven by the need of miniaturizing electronic devices and escalating its performance at the same time. The capability of controlling the chemical and physical properties of nanomaterials by controlling the size, shape, and composition at the nano-level provides the desired platform to archive efficient optoelectronic properties in demand. These significant chemical and physical properties of nanomaterials compared to its bulk material arises from the effect known as quantum confinement effect, which will be discussed later in this chapter.

According to Richard W. Siegel, nanomaterials are classified by their dimensionalities, zero, one, two, and three. Atomic clusters and cluster built ups such as nanoclusters and NPs portray zero dimensionality whereas the nanotubes, nanorods and nanofibers are one dimensional materials. In contrast, the nanofilms and layered nanosheets portray two dimensionalities while polycrystals and nanosized grains represents three dimensional materials.

Nanoscale materials can be produced in crystalline or amorphous phases and based on their electronic structure, they can be classified as semiconductors, metals, magnets, and insulating materials. These solids can be synthesized in different size and shape by precisely controlling the experimental parameters such as temperature, solvents, surfactants, and molar ratio of precursors. Because of widespread application, significant efforts have been devoted to production of nanoscale materials with competent physiochemical properties. Variety of applications, such as nanosized metallic powders (Fe, Ni) for coating and welding, magnetic particles (Fe₂O₃) for ferrofluids and information storage, metal oxide nanostructures, (FeO, NiO) for rechargeable batteries and dye sensitized solar cells, and semiconductors nanostructures (CdSe, ZnS, and
PbS$^{14}$ for optoelectronic devices, can be acclaimed from nanostructured materials. However, when considering electronic devices, optoelectronic properties of semiconductors summon our attention more than other physical or chemical properties.

### 1.2. Semiconductors

Since the era of nanomaterials became pronounced, semiconductor nanostructures received noteworthy attention compared to metals and insulators. To date, semiconductors are the most studied materials in the nanoworld and among many metal chalcogenides, Cd- and Pb- based chalcogenides are the most studied systems. They exhibit properties in between metals and insulating materials. Notably, semiconductors demonstrate distinct optical properties as a function of size and shape allowing the opportunity to tune its photophysical properties. Scientist have developed semiconductor nanocrystals for wide variety of applications such as bio-imaging and sensing, solar energy conversion, and a number of optoelectronic devices.$^{15}$

The unique photophysical characteristics of semiconductors arise from its bandgap and the potential to tune it as a function of size, shape and composition.$^{15}$ Electrons are located in the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LOMO) within a bond between two atoms.$^{16}$ As the bonding atoms accumulate closely, the energy levels merge along with its electron forming a continuous energy bands identified as the conduction band and the valance band. The HOMO energy levels create the conduction band whereas the LUMO levels accounts for valance band. The energy gap between the conduction and valance band level is known as the bandgap$^{15,17}$ (Figure 1.2). Materials usually fall in to three categories depending on its energy gap.
The bands overlap and a gap does not exist in metals. The electrons flow between bands and allows metals to be conductive.\(^{17}\) On the other hand, bands in semiconductors and insulators are not overlapped, creating a gap between HOMO-LUMO levels. If an electron need to be transferred across bands, the electrons should be excited by an external energy source.\(^{17}\) This excitation can be achieved fairly easily in semiconductor materials compared to insulators due to considerably lower bandgaps in semiconductors. Typically, bandgaps of semiconductor materials range between 0.2 -4.0 eV.\(^{2}\) Therefore, electrons can be excited across the energy gap by supplying heat or light. Due to the large energy gap in insulators (> 4.0 eV) the electron transition across the bandgap is prohibited. When semiconductor material receives sufficient energy more or equivalent to the bandgap, electrons can be excited to the conduction band using light energy (photons) leaving behind a positively charged hole in the valance band. The resultant electron-hole pair is generally known as the exciton in semiconductors (Figure 1.3).\(^{17}\)

Semiconductors are classified into two groups, direct and indirect depending on the nature of the bandgap.\(^{18}\) In direct gap semiconductors the valance band maximum and the conduction band minimum are aligned at the same momentum, so the excited electron can directly cross the energy gap to reach the conduction band edge. However, in indirect gap semiconductors the valance and conduction band maximum and minimum are in two different momenta of space so that the direct electronic transition is restricted.\(^{18}\) The electron transitions across the band in indirect bandgap semiconductors requires a phonon (lattice vibration). When the phonon is present the indirect bandgap can create an exciton generating important properties of the semiconductors, such as absorption and emission. The direct bandgap semiconductors exhibit high light absorption and emission
whereas the indirect-gap semiconductors are poor light absorbers/emitters. Thus, recent literature suggest that nanostructuring and composition tuning (i.e. alloying) in indirect-gap semiconductors can be utilized to optimize their photophysical properties.

**Figure 1.2.** An energy level diagram of bulk metals, semiconductors, and insulators.

**Figure 1.3.** Schematic diagram of a semiconductors demonstrating the generation of electron-hole pair (i.e. exciton) via photoexcitation process.
1.3. Quantum Confinement and Optical Properties of Nanoscale Semiconductor Materials

The Quantum confinement phenomenon is quite prominent in nanosized semiconductors and it is determined by the Bohr radius of the material. The Bohr radius is the distance an electron can travel from ground state energy level when excited. This excited electron leaves a positive hole behind in the valance band. This excited electron and the hole pair collectively together is an exciton. As the size of the material decrease below the Bohr radius, the space an exciton can travel become smaller than the Bohr radius. Such materials are considered to be quantum confined. As a result of decreased particle size, the energy bands become more discrete and band gap increases (Figure 1.4). According to the quantum confinement theory, the exciton has a finite distance. When the size of the semiconductor NPs is decreased below the Bohr radius, the charge carries could only travel within Bohr exciton diameter, which is within the quantum confined regime. This cause splitting of energy and increase in bandgap originating size dependent optical and electronic properties. Hence, the absorption and emission properties with distinct electronic transitions can be tuned by producing semiconductor NPs with different sizes and shapes. As the size of the NPs decreases a blue shift in absorption and emission is observed. Further, these semiconductor quantum dots can be engineered to gain higher quantum efficiency compared to bulk materials. This gain in high efficiency light emission known as radiative recombination rises due to the potential of strong overlap of the electron-hole pair as the quantum confinement effects are increased in semiconductor nanostructures.
Apart from the size, the shape of NPs also contributes to the quantum confinement effects. If the NP is symmetrical and larger, excitons can move in any direction. However, if the size is reduced to the quantum confinement level (i.e. below the excitonic Bohr radius) in one or more direction, changes in absorption and emission are observed.\textsuperscript{20} Depending on the dimensionality of the confinement, nanomaterials can be categorized as quantum wells, quantum wires, and quantum dots (Figure 1.5).\textsuperscript{20} The size is reduced in one direction in quantum wells allowing electrons to freely move in other two directions. Therefore, they are 2-D quantum confined nanostructures. In contrast, the size of the material is reduced in two directions in quantum wires allowing a 1-D confinement effect. When the size is reduced in all directions (i.e. quantum dots) resultant material exhibit 0-D confinement effects.\textsuperscript{20}

\textbf{Figure 1.4.} Size dependent electronic energy levels of semiconductors, from continuous bands in bulk to discrete molecular orbitals.
Figure 1.5. Geometries of nanoscale materials along with bulk crystalline solids (3-D), quantum well (2-D), quantum wire (1-D), and a quantum dot (0-D).

1.4 Plasmonic Metal Nanoparticles and Surface Plasmon Resonance

Metal NPs consist of transition metals and plasmonic metals elements such as silver (Ag), gold (Au), copper (Cu), and platinum (Pt) etc. They exhibit unique optical properties compared to other nanomaterials. The distinctive properties of the metal NPs have pronounced them as a great candidate for many applications in catalysis, electronics, and sensor development. For example, plasmonic Au nanorods can be embedded in to a DVD to increase the information density above $10^{12}$ bits per cm$^3$ (1 Tbitcm$^3$).\textsuperscript{20} The interaction between the electromagnetic field of light and electrons in metals are known as plasmonics.\textsuperscript{21} However, not all metals sustain the capability to interact with light. Thus far, Ag, Au, and Cu metals are identified as plasmonic metals. The oscillation of the free electrons in metals collectively in the presence of an external electromagnetic filed is known as the localized surface plasmon resonance (LSPR) (Figure 1.6).\textsuperscript{22} The location,
width, and the intensity of LSPR typically changes with the metal (Ag, Au or Cu), nanoparticle morphology, size, shape, composition (for alloys) as well as their environment.\textsuperscript{22}

In general, the surface plasmon resonance (SPR) of hollow Au and Ag NPs can be tuned within a wide range by controlling the outer diameter and wall thickness. It is reported that LSPR of Au nanoshells could be tuned from 550 – 820 nm\textsuperscript{23-24} for hollows with 24.5 - 44 nm outer diameter and 3 - 5.7 nm shell thickness. In contrast, for Ag hollow particles could also be tuned by controlling the shell thickness.\textsuperscript{25} LSPR of Ag nanoshells could be tuned from 470 – 570 nm with 24.1 – 60.1 nm outer diameter and 5.8 – 11.2 nm shell thickness.\textsuperscript{25} This unique tunability of LSPR can be used when coupling plasmonic metals with semiconductor NPs as the SPR could be tuned to overlap the excitonic energy of the visible semiconductor NPs.\textsuperscript{4}

\textbf{Figure 1.6.} A schematic illustration of the surface Plasmon resonance of Metal NPs.
1.5. Metal – Semiconductor Hybrids

Hybrid nanostructures are made by linking disparate materials into one system. For example, metal-semiconductor, semiconductor-semiconductor, and semiconductor-insulator nanomaterials can be coupled to produce novel hybrids. Construction of hybrid nanostructures provide the ability to bring chemically and physically similar and dissimilar constituents together to possibly make changes to their overall optical and electrical properties or altogether generate novel optoelectronic properties. Among, hybrid nanostructures, metal-semiconductor hybrids have received noteworthy interest because of the potential to couple electronic energy levels of chemically dissimilar constituents. Different assembly methods, such as layer by layer assembly and sol-gel method have been utilized to achieve a higher degree of control over their optical properties by tuning individual components as desired, to improve interfacial interactions. Further, hybrid nanostructures of metal-semiconductor can be composed to enhance the light-matter interactions of materials. Moreover, bottom-up colloidal synthesis techniques provides the highest control over many different synthetic parameters with the potential to produce optimized hybrid materials with unique physiochemical properties.

Changes in optical, and electrical properties, has been reported as a result of hybrid generation from variety of different materials. Recently, metal-semiconductor hybrid systems gained noteworthy attention over other hybrids due to their unique optoelectronic properties and tunability. Hybrid materials between metals and semiconductors allows the prospect of bringing distinct optical properties of plasmonic metals and semiconductors to coalesce. More importantly the integration of plasmonic metals with semiconductor NPs allows the coupling of high absorption cross sections and size-
tunable optical properties of semiconductor NPs, with the localized plasmonic resonance of metal NPs. To date, many metal-semiconductor hybrid systems have been developed utilizing plasmonic metals and semiconductors such as CdSe/Ag core/shell NPs, Au or Ag decorated CdS NPs, and Au, Ag, and Pt metals deposited on ZnO NPs.\textsuperscript{28}

Nonetheless, in many cases fluorescence quenching of the semiconductor was noted as the predominant effects due to higher metal loading and/or inability to tune interfacial interactions.\textsuperscript{4} Recently, our group reported the sol-gel derived CdSe-Ag hybrid aerogels with CdSe and Ag nanodots, where metal-semiconductor direct interfacial interactions are present. Which lead to generation of a novel radiative decay pathway.\textsuperscript{4} The generation of new emission is attributed to the precise control over interfacial interactions between the metal and the semiconductor components. Furthermore, it is of great interest to produce improve metal-semiconductor hybrid nanostructures for different applications and such hybrid materials could possibly lead to multifunctional materials in technology.\textsuperscript{29}

1.6. Synthesis of Nanoparticles

The synthesis of discrete nanomaterials with control over physical parameters is an important part in the nanoscience research as the chemical, physical, and optical properties are primarily governed by the size, shape, and composition of the synthesized particles. Synthesis is mainly categorized into two techniques: top-down and bottom-up.\textsuperscript{21} Top-down method utilizes an electron beam or an ion beam to physically break down bulk materials into desired sizes and shapes with some controllability. Variety of top-down synthesis techniques are used to produce NPs in many different shapes and morphologies.\textsuperscript{2} Mechanical milling, chemical etching and ion beam techniques are a few
examples of Top-down synthesis. However, the control over particle size and shape is comparatively limited and often results in polydispersed micro-to nano-sized particles.

In contrast, bottom-up assembly involves breaking down of bulk material into desired size and shapes utilizing chemical and physical methods followed by amalgamation of atoms into clusters and to particles by controlling the chemical and physical environment. Both bottom-up and top-down syntheses of NPs can be categorized in to physical and chemical methods. Physical methods include laser ablation, ultra-sonication, irradiation, microwave synthesis and ball milling. Chemical methods include electrochemical synthesis, colloidal synthesis, chemical vapor deposition and inert condensation method. However, laser ablation technique in top-down method and colloidal synthesis in bottom-up method, are more prevalent over other techniques in NP synthesis.

Laser ablation method is used to produce self-organized nanostructures on solids surfaces by irradiating a high-energy laser on the target surface inside a liquid medium. (Figure 1.7) Once the bulk material is broken down the ablated NPs can further react with the solution to modify the resulting NPs.
Among bottom-up approaches, colloidal synthesis has become one of the key developments in the advancement of nanoscience, as it places the ability to create size-/composition-/shape-controlled nanostructures in device-relevant quantities into the hands of nearly any researcher. It also, by default, creates nanocrystals that are amenable to a wide range of low-cost processing techniques. Since this is a wet chemical, solution based procedure, selectivity among different solutions, surfactants, precursors, pH, temperatures and pressures can be utilized to control the physical properties of resultant nanostructures. Water is commonly used in colloidal metal NP synthesis due its ability to provide a neutral reaction medium and its capability of dispersing as-prepared metal NPs. However, water is not the best solvent for semiconductor NP synthesis due to high temperature requirement above the boiling point of water to attain crystalline
materials. Thus, non-aqueous, high boiling point (300-350°C) organic solvents are typically used in semiconductor NP synthesis. The growth of NPs via colloidal synthesis is explained using La Mer style nucleation and growth mechanism (Figure 1.8).  

![Figure 1.8. La Mer style nucleation and growth mechanism in colloidal synthesis.](image)

In the above mechanism, first the precursors undergo nucleation, a process where the precursors decay and start to generate the new self-organized phase upon rapid injection of reactants at 150 – 350 °C temperature. Afterwards, the atomic precursors coalesce reducing the solution concentration until all the precursors are being used during the growth stage. The growth continuous and small crystals with higher energy dissolves into atoms to coalesce with larger crystals during Oswald ripening. During this stage the size
distribution is determined, monodispersity of particles achieved and the direction of growth is controlled to produce, rods, spheres, cubes, and many other shapes.²

Synthesis of semiconductors for the use of optical applications began many centuries ago when semiconductor pigments were used to produce stained glasses.⁴⁰-⁴² However, nowadays, semiconductor crystals are synthesized as an epitaxial structure or colloidal suspension. Epitaxial crystal structures provide the ability to synthesize wide variety of shapes and sizes with higher reproducibility and they can be used directly in optoelectronic devices.¹⁵ On the other hand, semiconductor crystals grown in colloidal suspensions allows incomparable control over shape, size, and monodispersity.¹⁵ Moreover, solution phase colloidal synthesis allows the ability to establish surfactant on the NP surface. This grants the ability to modify the surface as desired by the application requirements along with necessary absorption and emission properties by moderating the surfactant along with the tunability of size, shape, crystal structure and composition.

1.7. Sol-Gel Method and Aerogels

Sol-gel method is a well-known and widely used technique to create porous nanostructures of metal oxides and hydroxides.⁴³-⁴⁶ In 1846, Ebelmen accidently synthesized the first silica gel.⁴⁷ Since then the sol-gel process has been used to synthesize inorganic gels of different kinds of materials, such as SiO₂, Al₂O₃, and TiO₂. Materials are usually in solution before assembling in to a connected network. The sol then undergoes gelation, changing the solution into viscous medium creating a jelly-like jello material.
Sol-gel process of metal oxides consist of two steps, hydrolysis and condensation.\textsuperscript{43,45-46} During this process, metal alkoxides, M(OR)\textsubscript{n}, hydrolyze into hydroxylated metal centers (R.1) and hydroxylated metals expel water or alcohol to make oxy-polymers during condensation.\textsuperscript{43} Oxygen bridges in oxy-polymers, such as M-OH-M “ol” bridges or M-O-M “oxo” bridges connect NPs to make networks within gel structure.\textsuperscript{43}

\begin{align*}
\text{Hydrolysis} & : \quad M(OR)_n + H_2O \rightarrow (M(OR)_{n-1}(OH)) + ROH \quad \text{R.1} \\
\text{Condensation} & : \quad M-OH + M-OX \rightarrow M-O-M + XO(H) (X= H \text{ or } R) \quad \text{R.2}
\end{align*}

Drying of the wet-gels, via supercritical or conventional bench-top methods, produces the aerogel materials. Aerogels are porous inorganic polymers with high surface areas, low densities and large pores.\textsuperscript{14} Once the wet gel is produced, the aqueous solutions of the gel is removed by supercritical drying to create the aerogel. Supercritical drying allows the retention of porous gel network while the solution is being replace with air, so the resulting monolith structure is nearly similar to the wet gel structure. However, supercritical drying conditions, such as pressure, temperature, solvent and drying duration should be adjusted according to the material to obtain optimum porous structure and texture of the aerogels.\textsuperscript{43} To date, different types of aerogels have been identified, such as metal oxide (SiO\textsubscript{2}), metal (Ag, Au/Ag), organic/carbon (melamine-formaldehyde, MF), and semiconductor (CdS, CdSe, CdTe) aerogels.\textsuperscript{43} Metal oxide aerogels are currently used for cosmic dust collection, medium encapsulation, as additives, nuclear waste storage, and as catalysts.\textsuperscript{43}
1.8 Nanoparticle Condensation Strategy

Colloidal synthesis of metals and semiconductors generate monodispersed NPs in the solution medium. However, these NPs needed to be connected and converted into an aerogel without disturbing its 3-D network. Specially, metal chalcogenides NPs needed to be connected and separated from the aqueous medium for its further development for applications. As a result, nanoparticle condensation strategy has been developed and reported to be effective in assembling wide range of semiconductor NPs into chalcogenide gel materials.\textsuperscript{48-50} First, the NPs were synthesized with a passivated surface ligands and the surface functionalization (typically thiolates) will be systematically removed by oxidation creating low coordinated, active sites on the particle surface. The formed active sites are highly reactive allowing the NPs to establish direct interfacial linkages, polymerize into low dimensional (fractal) clusters, and consequently highly porous superstructures that augment the unique, nanoparticulate properties. The resultant aerogels are expected to exhibit optical transparency or opacity, high surface area and porosity, and superior electrical and thermal transport properties that can be manipulated by tuning the oxidation/reduction kinetics, colloidal aggregation mechanics, and size, shape, and composition of precursor NPs.

Resulting byproducts of the aforementioned oxidative gelation process can be removed by exchanging the solvent with water or acetone. Then, the wet gel can be either be dried supercritically or on a benchtop to produce NP monoliths \textit{i.e.} aerogels and xerogels, respectively. The aerogels will retain the 3D network of the wet gel. In contrast, when the gels are dried on the benchtop, uniquely porous structure collapses due to capillary forces creating dense xerogel materials (Figure 1.9).
Figure 1.9. A schematic representation of the NP condensation strategy to produce metal and/or semiconductor aerogel and xerogels.
Metal chalcogenides, such as metal sulfides (ZnS, CdS), metal selenides (CdSe, PdSe) and metal tellurides (CdTe, PbTe) are a well-known class of semiconductor NPs with size and shape dependent optoelectronic properties.\textsuperscript{51} The band gap energies of chalcogenide semiconductors range from ultra violet region to near infrared regions providing the opportunity to tune their optical properties within a wide energy range. Due to the tunability across the electromagnetic spectrum, metal chalcogenides are great contenders for wide variety of optoelectronic application such as bio-imaging, light emitting diodes, and optical sensing.\textsuperscript{52-54} Colloidally synthesized chalcogenide semiconductors has been successfully transformed into high surface area, highly porous, monolithic aerogel and xerogels, via nanoparticle condensation strategy, while retaining their unique quantum confined optical properties.
1.10 Thesis Statement

This research project is comprised with three primary goals. The first goal is to develop colloidal synthesis procedures to produce individual components, metal and semiconductor NPs, with overlapping plasmonic and excitonic energies. Second is to develop a new general methodology for metal-semiconductor NP assembly into hybrid nanostructures that exhibit direct interparticle connectivity, leading to tunneling of charge carriers from semiconductor to metal components. Finally, to utilize steady state and ultrafast absorption and emission spectroscopy to probe the optical properties of hybrid assembly and to investigate the key factors on the generation of novel, hybrid emission.

In order to achieve the first goal, the focus was put on synthesizing spherical shaped hollow Ag NPs, spherical shape CdSe and rod shaped CdSe. Despite, many synthetic procedures have been reported for Ag and CdSe, specific parameters were needed for the precise overlap of the Ag plasmon with CdSe exciton, while maintaining the quantum confined size within the visible spectrum. Secondly, the stabilization of surfactant ligands and their compatibility in the producing the desired hybrid nanostructure is the key for the success of this project. The CdSe NPs produced via colloidal synthesis are hydrophobic and the ligands should be exchanged with hydrophilic groups to be dispersed in hydrophilic solvents, as the Ag NPs are already produced under hydrophilic conditions. The first goal was achieved by synthesizing metal and semiconductor NPs counterparts with overlapping of plasmonic and excitonic energy by taking the advantage of control over size and shape by changing experimental parameters, surfactant, solutions, and their quantities. Many aspects of the reaction conditions were tested and repeated to assure the chosen parameters were preeminent. The hydrophobic ligands of CdSe were
then exchanged with mercaptoundecanoic acid to make it compatible with water for co-gelation of CdSe and Ag particles.

In order to achieve the second goal, the gelation kinetics of oxidation-induced self-assembly should be examined and the proper wet gel should be formed. Secondly, the supercritical drying method should be tested with different drying times to ensure the complete drying, while maintaining the unique porosity and the 3D nanostructure of the wet-gel. Since sol-gel method has been already used in generation of CdSe aerogels, it was expected that it would also be successful in creating the CdSe/Ag hybrid aerogels. However, gelation parameters should be optimized to produce hybrid nanostructures with different chemical constituents. Ability to control the interparticle interactions during gelation process was gained by coating NPs with thiolate ligands, where ligands maintained the stability and interparticle distance of NPs in solution.

The third goal is to identify and analyze the physical and photophysical properties of as-synthesized metal-semiconductor hybrids. According to the literature, it is expected that sol-gel derived hybrids exhibit novel optical properties as a result of direct interparticle connection between the chemically dissimilar constituents that are markedly different from their individual components. Thus, steady state and ultrafast absorption and emission spectroscopy has been employed to differentiate the optical properties of individual NPs and nano-hybrids. Finally, the generation of metal-semiconductor hybrids with novel and tunable physical properties will add to the overall tool-box of semiconductor aerogels with improved optical properties with the potential to enable efficient capture of light using both plasmonic metals and semiconductor nano-entities.
CHAPTER 2

EXPERIMENTAL METHODS AND MATERIALS CHARACTERIZATION TECHNIQUES

Metal-Semiconductor hybrid aerogels were prepared by sol-gel assembly of colloidal semiconductor and metal NPs followed by supercritical CO\textsubscript{2} drying. The resulting aerogels were characterized by diffuse reflectance UV-Visible spectroscopy (DR), photoluminescence (PL) spectroscopy, transmission electron microscopy (TEM), nitrogen adsorption/desorption surface area and porosimetry, powder X-ray diffraction (PXRD), and inductively coupled plasma optical emission spectrometry (ICP-OES). This chapter presents the chemical materials used in this research study, and experimental procedure for colloidal synthesis of metal and semiconductor NPs, sol-gel assembly of NPs into hybrid nanostructures, advanced material characterization techniques used to evaluate the physical and photophysical properties of Cd/Se/Ag hybrids.

2.1 Materials.

Cadmium oxide (CdO, 99%), silver nitrate (AgNO\textsubscript{3}, 99.9%), sodium borohydride (NaBH\textsubscript{4}, 98%), n-tetradecylphosphonic acid (TDPA, 97%), trioctylphosphine (TOP, 97%), and tetramethylammonium hydroxide pentahydrate (TMAOH, 97%) were purchased from Strem Chemicals. Triocylphosphine oxide (TOPO, 99%), 11-mercaptoundecanoic acid (MUA, 95%), tributylphosphine (TBP, 97%), toluene, L-glutathione reduced (98%), and tetranitromethane (TNM) were purchased from Sigma-Aldrich. Elemental Se (99%), ethyl acetate, methanol (99%), NaOH, and acetone (ACS grade) were purchased from Fisher
The water used in all syntheses was 18MΩ Mili-Q filtered water. All chemicals were used as received without further purification.

2.2 Experimental Techniques

2.2.1 Schlenk line Techniques.

Synthesis of CdSe NP involves a reaction between Cd\(^{2+}\) and Se\(^{2-}\). CdO precursor provides Cd\(^{2+}\) and Se powder in TOP or TBP solution provides Se\(^{2-}\). These syntheses are air sensitive and should be done under inert atmosphere. The Schlenk line techniques provide the required inert conditions for the synthesis of CdSe NRs and NPs. The Schlenk line apparatus consists of two apparatus and they are connected to the vacuum pump and an inert gas line separately (Figure 2.1). During the CdSe quantum dot synthesis, the reaction flasks with required materials are connected to the Schlenk line using a rubber tube and the flasks were degassed using the vacuum pump. A cold liquid N\(_2\) trap was used to protect the vacuum pump by condensing the generated solvent vapor and gaseous products. After degassing process is completed, the inert gas line was opened and the reaction flask was purged with either N\(_2\) or Ar. After purging, it is connected to an oil bubbler to maintain a steady flow of the inert gas.
2.2.2 Inert Atmosphere - Glove Box

A glove box with an inert atmosphere is used to store and process air and moisture sensitive chemicals. Normally, the glove box is completely sealed and the front side contains an observation window with arm-length rubber gloves attached. The reaction chemicals and materials are transferred in and out of the glove box through two (large and small) antechambers equipped with evacuation and refill controllers, vacuum pump and purge valves. An inert gas is continuously circulated through the glove box and molecular sieved are placed to eradicate O$_2$ and H$_2$O in order to maintain the required inert atmospheric conditions inside the box.
2.2.3 Supercritical CO\textsubscript{2} Drying

Supercritical drying (SCD) is an essential process in creating aerogels, where porous structure of the hydrogel will be retained without rupture or shrinkage while the solvent is replaced with air.\textsuperscript{43} During SCD process, liquid inside the hydrogel pores are replaced with air. However, if the hydrogel is air dried on a benchtop, as the solvent is being replaced by air during the sol-gel transformation process, the pores of the gel structure collapse due to capillary forces.\textsuperscript{43} The SCD method is used to overcome structural damages and to retain the original architecture of the hydrogels/wet gels. When the temperature of a closed vessel containing a liquid is increased, the density of the liquid decreases as the density and the vapor pressure of the air increases. At a certain temperature and pressure, the densities of the liquid and its vapor become equal. This intersection of the temperature and the pressure where the densities of the liquid and vapor are similar to each other is known as the critical point (Figure 2.1) of the liquid. At the critical point the gas/liquid boundary of phase change disappears and if the temperature and the pressure are further increased, a uniform solo phase, known as a supercritical fluid (Figure 2.2) is established. Supercritical fluids do not have surface tension due to the absence of a phase boundary between liquid and gas phases. Therefore, the supercritical liquid is able to escape the hydrogel without any structural damages to the porous infrastructure.\textsuperscript{45}

In this study, liquid CO\textsubscript{2} is used as the solvent during the SCD process. Liquid CO\textsubscript{2} reaches the supercritical fluid state above the critical point 31\textdegree{}C and 1050 psi.\textsuperscript{43} In a typical process, the wet hydrogels are transferred to a porous microcapsule and placed inside the critical point dryer and the chamber is filled with liquid CO\textsubscript{2} at 15 \textdegree{}C and ~900
psi. The liquid CO$_2$ in the chamber was exchanged five to six times over 12-24 hrs to ensure the complete replacement of the solvent (acetone) inside the hydrogel. The temperature and the pressure of the chamber is gradually increased to 40 °C and 1200 – 1400 psi, above the critical point temperature and pressure to form a supercritical fluid. The gels were left at 40 °C and 1200 – 1400 psi for 20 min to ensure the complete formation of supercritical fluid inside the critical point dryer. Finally, the supercritical fluid is released carefully over 25-30 min, resulting a monolithic aerogel. The temperature was maintained at 40 °C until venting is complete.

Figure 2.2. Phase Diagram of CO$_2$. Drying conditions of aerogels are shown by arrows.
2.3 Synthesis of CdSe Nanorods and Nanocrystals.

2.3.1 Synthesis of CdSe Nanorods.

CdSe NRs were synthesized using a previously reported procedure\textsuperscript{14} with slight modifications to scale up the synthesis. In a typical reaction for rod shaped CdSe, 0.0514 g of CdO, 0.2232 g of TDPA, and 3.7688 g of TOPO were degassed under vacuum at 100 °C for 30 min. The temperature was increased to 320 °C and the reaction was held under nitrogen flow for 16 hrs to produce a homogeneous colorless solution. In an air tight vial, 0.0316 g of Se was dissolved in 2 mL of TBP inside the nitrogen glovebox to produce a Se-TBP solution. The reaction temperature of the Cd-TDPA-TOPO mixture was reduced to 270 °C, and the Se-TBP precursor was injected immediately at 270 °C and the temperature was increased to 320 °C. TOPO capped CdSe NRs were grown at 320 °C for 6 hrs and isolated and purified by multistep dispersion and precipitation using toluene and methanol, respectively.

2.3.2 Synthesis of CdSe Nanocrystals.

CdSe nanocrystals were synthesized using a previously reported procedure\textsuperscript{14} with slight modifications to scale up the synthesis. In a typical reaction, 0.0514 g of CdO, 0.1116 g of TDPA, and 3.7688 g of TOPO were degassed under vacuum at 100 °C for 30 min. The temperature was increased to 320 °C and the reaction was held under nitrogen flow for 16 hrs to produce a homogeneous colorless solution. In an air-tight vial, 0.0316 g of Se was dissolved in 2.4 mL of TOP inside the nitrogen glovebox to produce
a Se-TOP solution. The reaction temperature of the Cd-TDPA-TOPO mixture was reduced to 270 °C, and the Se-TOP precursor was injected immediately at 270 °C and the reaction mixture was allowed to cool to 150 °C. Reaction was held at 150 °C for 15 min and the temperature was ramped by 10 °C/15 min until it reached 250 °C. TOPO-capped CdSe nanocrystals were grown at 250 °C for 4 hrs and isolated by multistep dispersion and precipitation using solvent/antisolvent mixture of toluene and methanol, respectively.

2.3.3 Surface Functionalization of CdSe with Thiolate Ligands.

TOPO-capped CdSe NRs and NPs were dispersed in 10 mL of 10mM MUA in methanol. The pH of the MUA solution was adjusted to 10 with TMAOH prior to addition of CdSe NPs. The solution was mixed well to ensure the ligand exchange. MUA-capped CdSe NPs were precipitated with ethyl acetate and dispersed in 10 mL of mili-Q H₂O to obtain MUA-capped CdSe sol.

2.4 Synthesis of Glutathiol Functionalized Ag Hollow Particles

Ag hollow NPs were synthesized using the literature method. In a typical reaction, 50 mL of Millipore water was added to a 250 mL round bottom flask and kept in the freezer for nearly an hour until ice cubes were formed on the surface. To this ice-cold water, silver nitrate (AgNO₃) (3 or 1 mL, 10 mM) and glutathione(GSH) (0.35 or 0.1 mL, 10 mM) were added. After ~4 minutes, sodium hydroxide (NaOH) (10 mL, 0.1 M) was poured into the above mixture with vigorous stirring. Then, a freshly prepared sodium borohydride
(NaBH₄) solution (3.6 mL, 10 mM) was quickly injected. The resulting mixture was stirred slowly (350 rpm) for nearly an hour to produce Ag hollow NPs.

In this synthesis, Ag₂O precursor seeds were prepared by reacting AgNO₃ with NaOH and Ag₂O was allowed to undergo chemical reduction with NaBH₄. The final concentration of the thiolate-coated Ag hollow NPs dispersed in Milli-Q filtered water is prepared to be 0.004 M. The size of the Ag hollow NPs was controlled by the added amounts of AgNO₃ and GSH. The added amounts of 10 mM AgNO₃ and GSH was 3 mL and 0.35 mL for Ag hollow LSPR between 490-505 nm and 1 mL and 0.1mL for LSPR between 515 - 530 nm respectively. The speed of NaBH₄ addition via Kirkendall-type reaction controlled the formation of the Ag hollow. The surface plasmon resonance (SPR) of prepared final Ag hollow NPs were at 490-505 nm and 515 - 530nm.

### 2.5 Synthesis of Metal-Semiconductor Hybrid Hydrogels and Aerogels.

CdSe NR solution was divided into 1 mL aliquots and varying volumes (10-500 µL) of GSH-coated Ag sol were added and mixed well to produce homogeneous solutions. To each vial of CdSe/Ag NPs, 50 µL of 1% C(NO₂)₄ was added to produce CdSe/Ag hydrogels. The solvent of the hydrogels was exchanged with Acetone 4 - 6 times over 4 - 5 days until a colorless sol was observed. The CdSe/Ag hydrogels were then transferred into porous microcapsules and loaded to the supercritical dryer (SCD) chamber at 15 °C. The SCD chamber was filled with liquid CO₂ and the liquid CO₂ was exchanged 5 - 6 times over 24 hrs. The wet gels were then dried supercritically at 40 °C for 28 min to yield monolithic CdSe/Ag hybrid aerogels.
2.6 Materials Characterization Techniques

2.6.1 UV-Visible spectroscopy

UV-Visible spectroscopy is one of the oldest and extensively used analytical techniques for probing optical transitions. Absorption properties of semiconductors, coordination complexes and conjugated organic compounds can be probed through UV-Visible spectroscopy. Generally, when visible or ultraviolet light travels through materials with chromophores, it can absorb the light to a certain degree. Due to this absorption, the incident light beam attenuates after passing through the material and the resulting transmitted light is detected by a detector generating an absorbance spectra. The amount of absorbed light energy is similar to the energy gap between the valence and conduction bands in the semiconductor materials. When light energy is being absorbed, the electrons are excited from the valance band to the conduction band and the onset of the generated absorption spectra can be used to measure the bandgap of the semiconductor. The energy above the onset value is related to the density of states. The absorption spectra for solutions were obtained by dissolving the solution of interest in optically transparent solutions such as, toluene and by collecting the absorbance measurements of the sample against the solvent reference. The amount and the path of the incident light is controlled by series of beam splitters and mirrors (Figure 2.3). As ultraviolet or visible light passes through the solutions and reach the detector, the transmitted light gets converted into absorbance value of the solutions. However, according to the Beer-Lambert law (equation 2.1), the absorption of sample (A), is directly proportional to the concentration (c), molar absorptivity (ε) of the solution and the path length (l) of the sample holder.
Absorption spectra for freshly prepared nanocrystals were collected soon after synthesis with toluene blank for CdSe NPs and diH₂O blank for Ag NPs. In this research study, all the solution based absorption measurements were collected in a Cary 6000i UV–vis–NIR double beam spectrophotometer (Agilent Technologies).

2.6.2 Solid State Diffuse Reflectance UV-Visible Spectroscopy

Diffuse reflectance spectroscopy is employed to analyze the absorption measurements of powdered, and nontransparent solids. When the incident light beam strikes a solid sample, part of it reflects from the surface and part of it transmits. The photons that interacts with the particles can transmit through the particle, and later, it can...
either be reflected off or transmitted to the next particle. However, the photons that are reflecting from the surface will be lost and is not integrated in the measurements. When the photon energy is transmitted, and penetrated through the particles continuously in the powdered solid sample, some portion of the photon energy can be absorbed. As this process continue multiple times, in due course, light will return back to the surface bearing optical information of the sample. \textsuperscript{59}

The Kubelka-Munk remission function (Equation 2.2) is applied to the percent reflectance measured from diffuse reflectance spectroscopy to obtain the pseudo-absorption of the solid material. \( R \) is the percentage diffuse reflectance of the analyte, which is equal to the ratio of molar absorption coefficient, \( K \), and the scattering coefficient, \( S \) in Kubelka-Munk remission function. \textsuperscript{60-61}

\[
f_{KM}(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S}
\] (2.2)

Generally, the reflected photons are collected by an integrating sphere (a spherical mirror) coated with 100\% reflecting substance, and are directed toward the detector to generate the diffuse reflectance measurement. In a typical procedure, powdered nanocrystals are homogeneously mounted over non-absorbing reflectance standard \( \text{BaSO}_4 \) (\( K=0 \) and \( R_{\text{std}} =1 \)) and the relative percent reflectance is measured.\textsuperscript{59} In this study, a Cary 6000i UV–vis–NIR spectrophotometer (Agilent Technologies) equipped with an internal DRA 2500 integrating sphere was used to measure the optical diffuse reflectance from 200 to 1800 nm. Collected reflectance data were translated to absorption by applying Kubelka-Munk remission function (Equation 2.2) and the band gap was obtained by extrapolating the absorption onset to the baseline of the spectrum.
2.6.3 Photoluminescence spectroscopy

The process of emission of light by excited electrons is referred to photoluminescence (PL), and the measuring and studying the processes of PL is known as PL spectroscopy. PL spectroscopy is commonly used for electronic structure analysis of semiconductor nanocrystals. The emission of light from excited states takes place due to the radiative recombination of the electron-hole pair generated by photo excitation. The radiative recombination of the electron-hole pair processes depends on the electronic state and can be categorized into fluorescence and phosphorescence, as depicted in Figure 2.4. In general, as semiconductor material absorbs light, an electron gets excited from the electronic ground state (So) (valance band) to the first singlet excited state (S1) (an excited state in the conduction band). This excited electron in the S1 vibrational level will release the absorbed energy by non-radiative processes, i.e. vibrations and rotations. However, fluorescence results when the excited electron in the excited singlet state falls back to the electronic ground state by emission of a photon. Phosphorescence results when an excited electron go on with intersystem crossing to an excited triplet state from the excited singlet before returning back to the electronic ground state. The life time of fluorescence is $10^{-4}$ to $10^{-9}$ s and phosphorescence is 100 to $10^{-3}$ s. Fluorescence is higher in intensity and shorter lived compared to phosphorescence. Usually, a red shift is observed for the emission wavelengths from the absorption energy due to non-radiative vibrational relaxations of excited electrons, which is known as Stokes shifts.
Figure 2.4. A schematic representation of the absorption and emission of light by photoluminescence processes fluorescence and phosphorescence.

In this research study, Cary Eclipse fluorescence spectrophotometer, Agilent Technologies with a xenon arc lamp that produces continuous wavelengths from 200 to 900 nm was used to gather photoluminescence properties of metal semiconductor hybrid aerogels.
2.6.4 Time-Resolved Photoluminescence (TRPL) Spectroscopy

Time-Resolved Photoluminescence (TRPL) Spectroscopy is employed to determine the emission decay, of the exciton electrons as a function of time. Generally, the emission process consists of radiative decay and when the electron-hole pair recombine and emit light, the excited electron falls back to the ground state. During this process, the electrons have the ability to change their emission pathways which can be probed by their decay times. The recombination life times are usually observed in microseconds, picoseconds, or nanoseconds using a streak camera, and the spectrum collected by TRPL is known as a streak image. TRPL measurements can also provide information about dominating recombination processes such as, radiative recombination and non-radiative recombination. The streak camera contains an ultra-high-speed detector to be able to capture the emission of light at extremely low time periods. However, due to its fast decay, it is difficult to reduce the background vibrations of the crystals at room temperature. Therefore, it is important to collect measurements at 77 K. The TRPL has the ability to operate from 5 K to 300 K. The source of the excitation is usually from Light Amplification by Stimulated Emission of Radiation (LASER) which is able to examine a range of emission relaxation pathways between wavelengths of 300 nm and 1500 nm.

In this research study, a Ti:sapphire laser was used to excite the NPs on a Si wafer at 15K utilizing a a Hamamatsu streak camera with a 25 ps temporal resolution.
2.6.5 Transmission electron microscopy

Transmission electron microscopic (TEM) technique is used to examine the morphology and the structure of nanomaterials. A monochromatic electron beam with a certain wavelength is generated by an electron gun and the beam is controlled by an applied electric field during sample examination and imaging. Usually, a tungsten filament crystal is used as the source of electron beams due to its ability to emit electrons with an applied electric field. This incident electron beam interacts with the sample and travels in different directions depending on the type of interaction with the nanomaterials (Figure 2.5).

Figure 2.5. Different events of incident electron beam after interacting with the sample
TEM analyzes nanomaterials by the transmitted electrons through a thin layer of the sample, and provide information regarding size, shape and morphology of the sample. Crystal structure of the nanomaterial can be identified by determining the lattice fringes through high resolution TEM with a resolution of 0.1 nm - 10 nm. The generated electron beam passes through a 200-400 keV accelerating voltage to acquire the needed energy to penetrate across the sample layer. A series of condenser lenses are used to focus the electron beam, and a condenser aperture is used for the electrons outside the optical axis. Then, the image is developed by a series of electromagnetic lenses.

In this project, a 10 µL of the dilute sample is deposited on a carbon coated copper grid and dried before imaging. A Zeiss Libra 120 with a Gatan ultrascan 4000 camera operating at 120 kV was used for low resolution imaging, and a FEI Titan 8300 electron microscope equipped with a Gatan 794 multiscan camera operating at 300 kV was used for high resolution imaging.

2.6.6 Powder X-ray diffraction

Powder X-ray diffraction (PXRD) technique is commonly used to identify crystallinity, phase and the structure of materials. The atoms are arranged in certain patterns in crystal structures and depending on the arrangement and distance of the atoms, different diffraction patterns are observed when a crystal is exposed to X-rays. The inter-atomic distance, the d spacing of the crystal structure is similar to the electromagnetic radiation wavelength of the X-rays, which is between 0.5 – 2.5 Å. Therefore, diffraction patterns unique to crystal structure/phases can be observed using x-rays. Though most of the crystal structures share similar unit cells and atomic arrangements, their bonding types
and elemental compositions are unique. Allowing it to generate a distinct pattern that serve as a fingerprint of individual structures. Hence, they can be used for fingerprint characterization of crystalline materials. Generally, an XRD instrument consist of an X-ray tube with a tungsten filament, a metal target composed of Mo, Cr, Co, Fe or Cu, a Beryllium window and a cooling system (Figure 2.6).

![Figure 2.6. Schematic diagram of a standard X-ray tube](image)

An electron beam is generated by flowing an accelerated voltage of 30 – 50 kV across a tungsten filament. The generated electron beam moves through the vacuum and bombards the surface of the metal target, ionizing its electron from 1s orbital (K shell), generating vacancies in the inner most shell of the metal atoms. The electrons from 2p (L shell) or 3p (M shell) moves in to the vacancy created in K shell. During this process, energy equivalence of either 1s-2p or 1s-3p is released as X-rays. The emitted wavelength and shell to shell transfer is constant for each element. Depending on the electron transfer between shells, two kinds of X-rays are being generated. If the electrons
fall from M shell to the K shell, Kβ radiation is generated and if the electrons fall from L shell to the K shell, Kα radiation is generated (Figure 2.7).

![Figure 2.7](image)

**Figure 2.7.** Illustration of electronic transitions between shells for X-ray radiation

Kβ radiation is very low in energy and do not provide sufficient energy to transpire out of the metal surface. However, Kα radiation contains sufficient energy to emerge out of the metal in all directions with a defined unique pattern to individual elements. A miniature opening with beryllium is used to let X-rays out from the X-ray tube to allow direction for X-rays. Beryllium is used due to its low X-ray cross section. The direction of the x-rays is important in maintaining the angle of incident in order to determine the atomic spacing otherwise known as the d spacing of the crystal structure. Scattering takes place in every direction as the X-rays strike the crystal structure. The X-rays scatter from the surface at
an angle equal to the angle of the incident rays or they can penetrate the crystal structure to inner planes. If the diffracted beams are out of phase when they overlap, the amplitude of the wave decreases and destructive interferences take place. If the beams are in phase with each beam when they overlap, the amplitude of the wave increases and constructive interferences take place.\(^6\) However, the distance the beams penetrate the crystal structure is solely dependent on the d-spacing of two consecutive planes inside the lattice structure.\(^6\) If we consider the diffraction of two beams, A and B (Figure 2.8), A diffracts as A' from the first plane and B diffracts as B', but B penetrates through the first plane and gets diffracted from the second plane of the crystal structure.

![Diagram](41)

**Figure 2.8.** Diffraction of X-rays from crystal planes

The distance between the diffracted planes is equal to the d-spacing of the lattice and the additional distance traveled by the beam B (XY + YZ) is equal to the integral of the wavelengths, \(n\lambda\). The diffraction angle \(\Theta\), which is known as the Bragg angle and the d-spacing of the lattice is related by Bragg’s law (Equation 2.3), where, \(\lambda\) is the wavelength.
of the X-ray, \( \Theta \) is the Bragg angle, the angle between the incident beam and the crystal surface, and \( d \) is the distance between planes.

\[
XY + YZ = n\lambda
\]

\[
\sin \Theta = \frac{XY}{d} = \frac{YZ}{d}
\]

\[
2 \sin \Theta = \frac{XY + YZ}{d} = \frac{n\lambda}{d}
\]

Therefore, \( n\lambda = 2d \sin \Theta \) \hspace{1cm} (2.3)

When the X-rays get diffracted from the crystals, a peak intensity can be observed and forms a unique pattern carrying information about the crystal structure as a result of constructive interferences. This peak intensity is plotted against \( 2\Theta \) to generate the PXRD patterns which provide specific information about the crystal unit cell, such as the size and shape. The peak intensity depends on how each atom is arranged in the unit cell, and different peak broadening can be observed, based upon the number of unit cells in the materials. Compared to bulk material, nanocrystals contain a few lattice planes and therefore, the X-ray beams do not undergo complete destructive interferences, which results in broader diffraction peaks. According to the Scherrer equation (Equation 2.4), the size of the crystallite is inversely proportional to the broadness of the peaks observed in PXRD patterns, where \( \lambda \) is the wavelength of the X-ray used, \( \Theta \) is the Bragg angle (diffraction angle), \( B \) is the full width at half maximum of the peak, and \( t \) is the size of the crystal.
\[ t = \frac{0.9 \lambda}{B \cos \theta} \quad (2.4) \]

In this research study, A Philips X’Pert system equipped with a Cu Kα monochromatic radiation with a wavelength of 1.5418 Å was used to record PXRD patterns of nanoparticles and aerogel materials. The Scherrer equation was used to determine the crystallite sizes.\(^{67}\) The powder samples were deposited on to a low background Si holder with a spinning stage. Collected X-ray diffraction patterns from aerogels were compared against the International Centre for Diffraction Data (ICDD) powder diffraction file (PDF) database to identify the crystal phases.

### 2.6.7 X-Ray Photoemission Spectroscopy (XPS)

X-ray Photoemission Spectroscopy (XPS) is one of the most powerful techniques for surface analysis of nanoscale material. XPS provides the elemental composition at the surface of the nanomaterials, bonding information, and the oxidation state of the elements present. XPS is also known as the Electron Spectroscopy for Chemical Analysis (ESCA). It is very critical to analyze the surface chemistry of the nanoparticle because of its high surface to volume ratios compared to other materials. However, XPS penetrates about 5-10 nm in to the materials and if the nanocrystal material that is being analyzed is smaller, the measurements of both surface and the bulk can be collected.\(^{68}\) A monoenergetic X-ray beam is bombarded on the sample to eject electrons from the surface atoms with specific energy levels. This energy required to eject electrons from the atomic orbitals are equal to the electron binding energy of the said element. The photoemission energy can be calculated by using the equation 2.5. \(E_{hv}\) represents the X-ray energy, \(E_{\Phi}\) is the work
function, $E_k$ is the photoelectron kinetic energy, and $E_B(i)$ is the electron binding energy on the specific level, according to the equation 2.5.

$$E_h \nu = E_k + E\Phi + E_B(i)$$  \hspace{1cm} (2.5)

Each element contains different binding energies and atomic structures and when they make a bond the surrounding binding chemical environment can change. This results in different oxidation numbers, less shielding effects on core electrons and increased binding energy. This binding energy is also influenced by electronegativity of the surface ligands and coordination effects of the bound elements. Thus, XPS is a vital analytical technique for the investigation of the surface properties of metals and semiconductors. The X-rays are generated using an X-ray tube (Figure 2.9) and were bombarded on to the surface of the sample under ultra-high vacuum to warrant accurate measurements.

**Figure 2.9.** Diagram of the X-ray photoelectron spectrometer and the hemispherical detector.\textsuperscript{67}
In this research study, a Thermofisher ESCALAB 250 XPS instrument equipped with an Al Kα source was used to collect XPS spectra of metal and semiconductor nanostructures. Samples were placed on a piece indium foil deposited on conducting carbon tape. The conducting carbon tape was used to account for the surface charging effect of the instrument to reduce any shifts in the binding energy. Al Kα produces narrow line width, high energy X-ray beams, and Al Kα is commonly used as the X-ray source in XPS. The collected XPS spectra is comprised with peaks denoting different binding energies of the elements present in the material surface.

### 2.6.8 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Inductively coupled plasma optical emission spectrometry (ICP-OES) is used to determine the elemental compositions of materials. ICP-OES is one of the most popular instruments for the trace element determination due to its ability to detect significantly low amounts of element present in samples. When measuring the elemental composition of CdSe/Ag metal semiconductor aerogels via SEM-EDS mapping, the energy of Cd and Ag overlap and cannot be differentiated. Therefore, the elemental composition analysis of CdSe/Ag was also done by employing ICP-OES.

The ICP-OES has the ability to detect multiple elements accurately at very low concentrations due to its high sensitivity to elements and depending on the analyte, measurements can be taken in parts per-millions to parts-per trillions. This instrument usually operates based on spontaneous emission of photons from the atoms and ions in the samples. Liquid and gaseous samples are introduced into ICP-OES by injection.
whereas, the solid samples require an acid digestion.\(^6\) CdSe/Ag metal semiconductor aerogels were digested in 10\% nitric acid at 100 °C for an hour to ensure its complete solubility in nitric acid, which allows the analytes, Cd, Se and Ag to be extant in a solution of nitric acid. Digested aerogels in 10\% nitric acid were diluted to have approximately 1 ppm and then introduced to the ICP-OES. The analyte solutions were converted in to aerosols and then introduced to a channel of plasma. The temperature at the core of the inductively coupled plasma is nearly 10,000 K and the aerosols are swiftly vaporized.\(^6\) The vaporized atoms gain energy by colliding with plasma imparts and converts them to ions.\(^6\) Thereafter, the ions continue to collide, and promotes their electrons to the excited states. Both excited atoms and ions relaxes down to the ground state by emitting photons.\(^6\) The concentration of the originating element in the CdSe/Ag aerogel samples are directly proportional to the total number of photons.

In this research study, the ICP-OES studies of CdSe/Ag aerogels were performed on a Varian 820 MS utilizing Cd, Se, and Ag standards with five different standard concentrations.
2.6.9 Surface Area and Porosimetry Analysis: Nitrogen Adsorption-Desorption Isotherms.

Gas sorption is known as the inclination of solid surfaces to draw gas molecules from its surroundings. The gas sorption process depends on the characteristics of the solid surface and can be used to examine the pore size and the surface area of materials. In this process the surface is the adsorbent and the gas molecules are the adsorbate.\textsuperscript{70}

The gas molecules and the surface interacts, this interaction can arise from either valence forces or Vander Waal forces.\textsuperscript{70} When valence forces are engaged, chemical bonds are made between the gas molecules and the surface, the adsorbent and the adsorbate, which is known as chemical adsorption or chemisorption.\textsuperscript{70-71} Not only valence forces, but also Vander Waal intermolecular forces can also contribute to the interaction of gas molecules between the adsorbent and the adsorbate, which is known as physical adsorption or physisorption.\textsuperscript{70-71} These, chemisorption and physisorption properties of the surface and gases was utilized to measure and analyze the area and the porosity of nanomaterials.

Adsorption isotherms are used to study the processes of adsorption. Isotherms are generated by measuring the changes of the gas volume and the relative pressure of the surface at constant temperature.\textsuperscript{70} The relationship between the volume of adsorbed gas (\text{cm}^3/\text{g}) and the relative pressure between the saturation pressure of the adsorbate and equilibrium (P/P\textsubscript{o}) is displayed in adsorption isotherms.\textsuperscript{71} When measuring the surface area and porosity, the nanomaterials should be degassed to ensure the surfaces are free of any gas molecules. Then the sample holder is filled with N\textsubscript{2}, inert gas at low pressure
pores <2 nm, micropores are being filled and as the relative pressure increased a monolayer of gas molecules are formed. Many layers of gas molecules are adsorbed to the surface and the pores of 2 – 50 nm (mesopores) and > 50 nm (macropores) are filled with the increasing relative pressure until the capillary condensation occurs\(^7\) (Figure 2.10).

Depending on the shape of the adsorption/desorption isotherms, they are categorized into six types (I – VI)\(^7\) (Figure 2.11). Type I isotherms are generated when small external surfaces exist on the microporous structure.\(^7\) Type II isotherms are generated when the surface is non-porous or without the presence of microporous.\(^7\) Type III isotherm is a result of weak adsorbent-adsorbate interactions.\(^7\) Type IV isotherms are generated when capillary condensation takes place in mesoporous.\(^7\) Type V isotherms are a result of weak adsorbent-adsorbate, thus different porous adsorbents compared to Type III.\(^7\)

Type VI is generated when stepwise adsorption takes place on a uniform non-porous layered surfaces.\(^7\) Usually, isotherms will contain hysteresis loops owing to the rates of pore filling and evacuation by the gas molecules bearing information about the pores on the material surface.\(^7\) There are four types of hysteresis loops, H1, H2, H3, and H4 (Figure 2.12). H1 and H4 corresponding to the two extreme types of multilayer range with higher capillary condensation within the mesopores structure.\(^7\) H2 and H3 are more intermediated compared to H1 and H4.\(^7\) H1 loop is often a result of agglomerated or very compacted spheres arranged in a uniform manner.\(^7\) H2 arises when the distribution of pore sizes and shapes are not uniform or well identified.\(^7\) Presence of plate-like particles with slit-shaped pores generate H3 type hysteresis.\(^7\) H4 type loops are generated from narrow slit-like pores in the material.\(^7\) Once the isotherm is recorded the surface area
and the pore size distribution can be computed by applying the Langmuir theory for chemisorption on the material surface. Materials with multilayer adsorption, physisorption and surfaces with mesopores are evaluated by applying Brunauer, Emmett, and Teller (BET) theory by applying the BET equation (Equation 2.6).

![Figure 2.10](image)

**Figure 2.10.** Adsorption (black)/desorption (blue) isotherm of a porous solid displaying the areas of the adsorption and desorption, micropore filling (I), monolayer formed (II), multilayer adsorption (III), pore filling (IV), and capillary condensation (V).
Figure 2.11. Six types of adsorption isotherms\textsuperscript{72}
The equilibrium and saturation pressure of the adsorbate is noted as $P$ and $P_0$, volume of gas adsorbed at a given relative pressure ($P/P_0$) is $V_a$, volume of gas required for monolayer coverage is $V_m$ and the constant is $C$. If BET equation is related to $Y = MX+C$ and a graph is created between $P/[V_a(P_0−P)]$ and $P/P_0$ ($Y$ and $X$), $V_m$ can be calculated by the slope and constant $C$ by the intercept of the graph.$^{71}$

$$\frac{P}{V_a (P_0−P)} = \frac{C−1}{V_mC} \frac{P}{P_0} + \frac{1}{V_mC} \quad (2.6)$$

Figure 2.12. Four types of hysteresis loops$^{71}$
The Barrett, Joyner, and Halenda (BJH) theory is applied to the isotherm to compute the distribution of the pores, average pore diameters and volumes.\textsuperscript{71} The BJH theory employs the Kelvin equation (Equation 2.7) to compute the pore size and its size distribution.

\[
\ln \frac{P^*}{P_0} = \frac{2\gamma \mu \cos \theta}{R T r_m} \tag{2.7}
\]

Critical condensation and saturation pressure is denoted by \(P^*\) and \(P_0\), \(\gamma\) is the surface tension, \(\mu\) is the molar volume of the condensed adsorbate, \(\theta\) is the contact angle of the solid and the condensed phase, \(r_m\) is the mean radius of curvature, absolute temperature \(T\) and the ideal gas constant \(R\).\textsuperscript{71} The mean radius of the curvature, \(r_m\) can be modified by \(r\), the pore radius and \(t\), the thickness of the surface since the gas is being desorbed from pores represents its volume. Therefore, the thickness can be calculated using the following equation 2.8, where, \(A\) and \(B\) represents the slope and the intercept of the graph between \(\log_{10} (P/P_0)\) and \(1/V_a\).\textsuperscript{71}

\[
t = \left[ \frac{A}{B - \log_{10} (P/P_0)} \right] \tag{2.8}
\]

In this research study, N\(_2\) adsorption/desorption isotherms were collected using Micromeritics ASAP 2020 surface area and porosimetry analyzer at 77 K. All samples were degassed under vacuum at 50°C for 24 h before the analysis. The surface area of the CdSe and CdSe/Ag hybrid aerogels were calculated by using the BET model and the average pore volumes and diameters were calculated by using the BJH model.
CHAPTER 3

RESULTS AND DISCUSSION

Development of metal-semiconductor hybrids have received great interest by scientific community due to its potential in efficient light harvesting, photocatalysis, and biomedical applications. In this research study, two metal-semiconductor hybrid systems were investigated. The first system is fabricated with a CdSe semiconductor nanorods (NRs) and Ag hollow nanoparticle (NPs) whereas the second system is composed of spherical shape CdSe semiconductor NPs and Ag hollow NPs. In the first system, the second exciton of the rod shaped CdSe was integrated with LSPR of spherical Ag hollow NPs whereas in the second system, first exciton of spherical CdSe was intergraded with the LSPR of the spherical Ag hollow NPs. The optical and physical properties of individual NPs were carefully examined and the hybrids were produced by utilizing the co-gelation of metal-semiconductor components, which has been proven to efficiently intermix the electronic states. 

As-synthesized hydrogels were dried via supercritical drying to produce porous CdSe/Ag aerogels. Luminescent CdSe NPs, NRs, and plasmonic Ag hollow NPs were produced by literature methods. Absorption and emission spectra of CdSe NPs exhibit first excitonic maxima at 515-530 nm, second excitonic absorption at 400-415 nm, and band edge luminescence at 555 nm (Figure 3.1a). The Absorption and emission properties of CdSe NRs show first excitonic peak at 595-605 nm, second excitonic peak at 490-505 nm, and band edge emission at 625 nm (Figure 3.1b). Compared to bulk CdSe, a higher blue shift in energy is observed for spherical shaped CdSe particles and
a smaller blue shift in energy is observed for rod shaped CdSe particles. This is attributed to the fact that dots are being confined in all directions (3-D) whereas the rods are being confined in one direction (1-D). As such, a higher energy blue shift in absorption and emission is expected for CdSe quantum dots.

The synthesis of hydrophobic, triocylphosphine oxide (TOPO) capped CdSe NRs and NPs were performed using the high temperature arrested precipitation reactions. The stabilization of the TOPO capped CdSe particles was maintained by interactions between P=O functional group of TOPO and the surface bound Cd$^{2+}$ species. To attain semiconductors with high crystallinity and improved optical properties, high temperature colloidal synthesis has been employed, where organic solvent/ligands with higher boiling points are used. Resulting TOPO capped CdSe particles were dispersible in nonpolar solvent (toluene, hexane) whereas the thiolate capped Ag NPs were dispersible in water, a polar solvent. To facilitate gelation in polar solvent media, TOPO ligands of CdSe NR/NPs were exchanged with 11- mercaptoundecanoic acid (Scheme 3.1) at pH ~ 10 adjusted with tetramethylammonium hydroxide (TMAOH). Resulting thiolate capped CdSe NRs/NPs were hydrophilic and can be readily dispersed in a number of polar solvents (water, ethanol, and acetone).
Efficient overlap of the CdSe excitonic absorption and the LSPR of Ag hollow nanoparticles is achieved by tuning the outer diameter and shell thickness of Ag NPs. During the synthesis, AgNO$_3$ was reacted with NaOH to produce Ag$_2$O NPs. These Ag$_2$O NPs were then reduced with NaBH$_4$ to produce Ag hollow NPs. The outer diameter of the Ag hollow NPs was tuned by adjusting the molar ratio of AgNO$_3$/GSH whereas the shell thickness of Ag nanoshells can be tuned to desired plasmonic energy by changing the concentration of AgNO$_3$ and GSH. In general, red shifting of the Plasmon band can be obtain by reducing AgNO$_3$ or GSH employed in the reaction. 3 mL of 10 mM AgNO$_3$ and 0.35 mL of 10 mM GSH was used to produced Ag hollow NPs with LSPR at 490 - 500 nm and 1 mL whereas 0.1 mL of 10 mM AgNO$_3$ and 0.35 mL of 10 mM GSH was used to synthesis Ag nanoshells with LSPR at 515 - 530 nm. The conversion of Ag$_2$O in to Ag hollow NPs was elicited by fast outward and slow inward diffusion of Ag$^+$ and NaBH$_4$ via Kirkendall-type reaction. In general, slow addition of NaBH$_4$ resulted in solid Ag NPs with LSPR at 400-410 nm whereas the fast addition of NaBH$_4$ produced Ag hollow NPs with varying shell thickness and size tunable plasmonic maxima of 470 - 570 nm.
The concentration of the resulting MUA capped CdSe colloidal sol was 0.04 M and GSH coated Ag hollow NP solution was 0.004 M. The high absorption cross section of the first excitonic energy of CdSe NPs was overlapped with the LSPR of Ag hollow NPs at ~520 nm (Figure 3.2a). The high absorption cross section of the second excitonic energy of CdSe NRs was overlapped with the LSPR of Ag hollow NPs at ~500 nm (Figure 3.2b).

The nanoscopic dimensions of the as-prepared NRs and NPs were characterized through transition electron microscopy (TEM, Figure 3.3). The average diameter of CdSe NPs was 3.9 ± 0.8 nm and the length of CdSe NRs was 17 ± 4 nm. The outer diameter of Ag hollow NPs were ~40-50 nm and shell thickness were ~9-11 nm. The morphology of individual NPs are significantly important when assembling into complex macroscopic hetero-structures via co-gelation as the optical properties are govern by the size and the shape of NP colloids. As the size of the particle increases the absorption maxima and the emission energy shows a red shift. Thus, the required size and the shape of individual NPs were controlled by changing the growth temperature, time, and utilizing coordinating solvents such as TOPO, TOP, and TBP. These coordinating solvents with high boiling point has the ability to control the particle growth. In this research study, TOPO and TOP was used in the synthesis of CdSe NPs as TOP influences the growth in spherical shape whereas the TBP directs the NP growth in longitudinal direction.
Figure 3.1. UV-Vis absorption spectra of CdSe NPs (a) and CdSe NRs (b) demonstrating the first and second excitonic transitions (red) and photoluminescence spectra demonstrating band edge emission (blue).

Figure 3.2. The normalized UV-Vis absorption spectra of CdSe NPs (red) and Ag hollows (green) demonstrating the overlap of the first excitonic absorption of CdSe NPs with the plasmonic resonance of Ag hollow NPs [a], CdSe NRs (red) and Ag hollows (green)
demonstrating the overlap of the second excitonic absorption of CdSe NRs with the plasmonic resonance of Ag hollow NPS [b].

The concentrations of as prepared CdSe NR and NP sols were determined assuming a 100% yield based on the molar amounts of the CdO precursor used in the synthesis whereas the concentration of Ag hollow NP sol was determined assuming a 100% yield based on the molar amounts of AgNO₃ used in the synthesis.

Total mass of CdO = 0.0514g
Total number of CdO moles = 0.0514 g/128.41 g moles⁻¹ = 4.00 x 10⁻⁴ moles
Total number of CdO moles = Total number of CdSe moles
Total number of CdSe moles = 4.00 x 10⁻⁴ moles
Thiolate-coated CdSe NRs and NPs were dispersed in 10 mL of ultra-pure Millipore water
Therefore, the concentration of CdSe NRs and NPs sol = 4.00 x 10⁻⁴ moles / 10 x 10⁻³ L

= 0.04 M

Concentration of the stock AgNO₃ solution = 1 x 10⁻² M
Volume of the stock AgNO₃ solution = 4 mL
Total number of Ag moles = 1 x 10⁻² moles/L x 4 x 10⁻³ L = 4 x 10⁻⁵ moles
GSH coated Ag hollow NPs were dispersed in 10 mL of ultra-pure Millipore water
Therefore, the concentration of Ag hollow NPs sol = 4 x 10⁻⁵ moles / 10 x 10⁻³ L

= 0.004 M
For NPs passivated with organic ligands, the organic coating layer provides stability in solution as well as the possibility of tuning the interfacial interactions. However, oxidation-induced self-assembly of thiol-coated metal and semiconductor NPs can be utilized to gain better control over the interfacial interactions.\textsuperscript{4, 14, 49, 77} The ideal overlap of the CdSe exciton and LSPR of Ag NPs were recently reported from our group by employing this method.\textsuperscript{4} In the current study, this strategy has been extended for the co-gelation of CdSe semiconductor NRs and NPs with Ag hollow NPs.

For co-gelation, appropriate amounts of Ag hollow NPs were mixed with CdSe NPs or NRs and C(NO\textsubscript{2})\textsubscript{4} was added. C(NO\textsubscript{2})\textsubscript{4} is non-oxigen transfer oxidant and able to oxidize thiolates without the oxidation of particles.\textsuperscript{48} In this process, surface bound thiol moieties oxidize into sulfenyl nitrates, which reacts with another thiol moiety to produce disulfides as shown in equation 1 and 2.\textsuperscript{78} As the thiolate ligands are removed, highly reactive surface sites are created, inducing an attraction between the metal and semiconductor particles. This leads to physical connection between the metal and the semiconductor NPs creating a “jelly-like” CdSe/Ag hybrid (hydrogel).

\begin{align*}
\text{RSH} + \text{C(NO}_2\text{)}_\text{4} & \rightarrow \text{RS(NO)}_2 + \text{C(NO}_2\text{)}_3^- + \text{H}^+ \\
\text{RSH} + \text{RS(NO)}_2 & \rightarrow \text{RS-SR} + \text{NO}_2^- + \text{H}^+ 
\end{align*}
Scheme 3.2. Representation of oxidation-induced direct cross linking of thiolate functionalized CdSe and Ag NPs to produce NP network of CdSe/Ag hybrids.

The gelation kinetics can be controlled by varying the amount of C(NO$_2$)$_4$ used. Typically, 50 µL of 1% C(NO$_2$)$_4$ provided moderate conditions for gelation resulting in an optimal hydrogel within one to two hours. Once the wet gel is produced, the byproducts of the oxidation was removed carefully by exchanging the supernatant solution with acetone 5 – 8 times over a period of 2 – 3 days. Finally, the acetone exchanged wet-gels were dried under supercritical conditions to produce CdSe/Ag hybrid aerogels.
Figure 3.3. TEM images of the (A) CdSe NPs, (B) CdSe NRs, and Ag hollow NPs with LSPR at (C) 500 nm, (D) 515nm used in the synthesis of CdSe/Ag hybrids.
Figure 3.4. Photographs of CdSe nanorods/Ag hydrogels [A] with varying Ag content: (a) 0, (b) 0.2%, (c) 0.5%, (d) 0.7%, and (e) 1%, CdSe nanoparticles/Ag hydrogels [B] with varying Ag content: (f) 0, (g) 0.2%, (h) 0.5%, (i) 0.7%, and (j) 1%.

Figure 3.5. Photographs of CdSe nanorods/Ag hydrogels with varying Ag content: (a) 0, (b) 0.2%, (c) 0.5%, (d) 0.7%, and (e) 1% under UV light.
Figure 3.6. Photographs of selected CdSe/Ag aerogel monoliths with 1% Ag loading. Top view [A] and side view [B]. Scale bar is in centimeters.

Monolithic CdSe/Ag aerogels were weighed, and the height/diameter was measured to determine the density (Table 3.1). The density of the hybrids increases with increasing amounts of Ag due to slower gelation rate as the oxidation kinetics of CdSe – MUA and Ag – GSH, surface thiolates are different.\(^4\) Longer gelation times were observed with addition of higher Ag amounts into CdSe NP sols, which resulted in significant compaction and syneresis of the wet-gels yielding CdSe/Ag hybrids with higher densities.

The color of the aerogels darkened as the amount of Ag increased. Typically, electron cloud in metal aerogels (Ag, Au, and Au/Ag) absorbs wide range of visible light and display black color.\(^74\) On the other hand, CdSe NPs can be tuned to portray wide range of colors from yellow, orange, to deep red. As prepared CdSe dots were orange color (Figure 3.4[B]) due to the fact that first excitonic absorption observed at 515 – 530 nm. In contrast, CdSe NRs were deep red color (Figure 3.4[A]) owing to first excitonic absorption at 595-605 nm. Since Ag metal absorbs all light, when mix to generate the hybrid, the
orange-red color of the CdSe NPs/NRs is being over taken by the Ag NPs. Therefore, as the Ag amount increased the color of the monolith darkened (Figure 3.4 and 3.5). Since the rod shaped CdSe is deep brownish red, the color change due to loading of Ag was not clearly visible to the naked eye but it was observable under UV light (Figure 3.5).

Table 3.1. The densities of CdSe nanorods/Ag aerogels with varying Ag content: (a) 0, (b) 0.2%, (c) 0.5%, (d) 0.7%, and (e) 1%. The elemental compositions were calculated according to the amount of precursor used in the synthesis assuming a 100% yield.

<table>
<thead>
<tr>
<th>Amount of Ag (%) in CdSe hybrid aerogels</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.014</td>
</tr>
<tr>
<td>0.2</td>
<td>0.017</td>
</tr>
<tr>
<td>0.5</td>
<td>0.021</td>
</tr>
<tr>
<td>0.7</td>
<td>0.023</td>
</tr>
<tr>
<td>1</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Low-resolution TEM images of hybrid aerogels suggest the three-dimensional connectivity of the NPs. The dark contrast areas represent multiple layers of the aerogel depicting a 3-D network. The TEM images of rod shaped CdSe/Ag gel exhibit a similar three-dimensional connectivity, with open fractal structure. However, due to contrast and thickness of the layers, Ag hollows were not visible in aerogels assembled with rod shaped CdSe and Ag hollow NPs (Figure 3.7). Nonetheless, both gel structures exhibit a large number of mesopores and macropores throughout the gel materials.
Figure 3.7. Low resolution TEM images of (A) spherical shaped CdSe/Ag aerogel and (B) rod shaped CdSe/Ag aerogel. Dark contrast areas show the 3-D nature of the materials.
The surface area of rod shaped CdSe and CdSe/Ag hybrid aerogels were obtained by applying the Brunauer-Emmett-Teller (BET) model to nitrogen adsorption/desorption isotherms (Figure 3.8 and 3.9). In general, combination of Type IV and II isotherm curves were obtained indicating the formation of meso-to-macro-porous aerogel. The hysteresis loop with H3 character was obtained for rod shaped CdSe aerogels indicating the presence of slit shaped pores.\textsuperscript{14} The BET surface area of the aerogels produced from CdSe rods without Ag was 136 m\textsuperscript{2}/g and with 0.5\% of Ag was 86 m\textsuperscript{2}/g. The average pore diameters of the rod shaped CdSe aerogels were approximately 30 nm (Figure 3.9[A] and 3.9[B]). In contrast, a surface area of 216 m\textsuperscript{2}/g and average pore diameter of 25 nm for CdSe NP aerogels whereas a surface area of 102 m\textsuperscript{2}/g and pore diameter of 35 nm was obtained for CdSe NP gels containing 0.5\% Ag (Figure 3.8[A] and 3.8[B]). A significant reduction in BET surface area was observed with Ag loading due to densification of the gel structure. As the amount of Ag is increased, longer gelation times were observed, which leads to solvent expulsion and compaction of wet gels creating dense monoliths resulting in lower surface area for aerogels containing Ag NPs.\textsuperscript{4,77}
Figure 3.8. Representative nitrogen adsorption/desorption isotherm (blue) of spherical shaped CdSe and corresponding BJH pore size distribution (red) [A], and isotherm (blue) of spherical shaped CdSe with 0.5% Ag loading and pore size distribution (red) [B].
Figure 3.9. Representative nitrogen adsorption/desorption isotherm (blue) of rod shaped CdSe and corresponding BJH pore size distribution (red) [A], and isotherm (blue) of rod shaped CdSe with 0.5% Ag loading and pore size distribution (red) [B].
Powder X-ray diffraction (PXRD) was utilized to probe the crystallinity and structure of the hybrid aerogels (Figure 3.10). The collected diffraction patterns of the hybrids displayed the hexagonal crystal structure of CdSe. However, the Bragg reflections corresponding to cubic Ag were not detected in CdSe/Ag aerogels composed of rod shaped CdSe, due to low concentration of Ag employed in the synthesis. In contrast, characteristic peaks of cubic Ag were identified in aerogels composed of spherical shaped CdSe when Ag content is greater than 50%. This observation is consistent with the previously reported data, where the cubic Ag pattern was not observed when Ag concentration in the CdSe gel framework is below 2%. Nonetheless, presence of CdSe-Ag NPs was confirmed by high resolution TEM analysis of CdSe/Ag hybrids with Ag concentration 0.1-2%. Thus, similar scenario can be expected for hybrids aerogels produced in this work.
Figure 3.10. PXRD Pattern of CdSe NP (A) and NR (B) aerogel (red), ICDD-PDF overlays of hexagonal CdSe (PDF # 08-0459, black) and Ag hollow aerogel (blue), cubic Ag (PDF # 01-0870-719, gray) are shown as vertical black lines.
Surface ligands of the NPs are removed via chemical oxidation, during gelation, to create active sites on the surface. When metal and semiconductor particles come in contact, surface $\text{Se}^{2-}$ can binds to the Ag metal (or $\text{Ag}^+$) creating the semiconductor-metal direct interfacial bond. The binding energies CdSe and CdSe/Ag was obtained from X-ray photoelectron spectroscopy (XPS, Figure 3.11 and 3.12). Binding energy of 405.2 eV (Cd 3d$_{5/2}$), 411.8 eV (Cd 3d$_{3/2}$) and 54.3 eV (Se 3d$_{5/2}$ and 3d$_{3/2}$) suggested the presence of Cd$^{2+}$ and Se$^{2-}$ in CdSe aerogels and further 54.3 eV of Se 3d supported the presence of reduced surface state of Se, $\text{Se}_n^{n-}$, which has been reported to bond CdSe NPs together in to fractal gel framework.\textsuperscript{79} The binding energies of CdSe/Ag hybrids were 404.9 eV (Cd 3d$_{5/2}$), 411.6 eV (Cd 3d$_{3/2}$), 54.1 eV (Se 3d$_{5/2}$ and 3d$_{3/2}$), 59.0 eV (Se 3d$_{5/2}$), 367.7 eV (Ag 3d$_{5/2}$) and 373.9 eV (Ag 3d$_{3/2}$). A 59.0 eV (Se 3d$_{5/2}$) surface state suggest the presence of SeO$_2$ which could result from the oxidative gelation process that takes place in water. Similar binding energies of Se 3d in CdSe as well as CdSe/Ag hybrids suggested the absence of cation exchange between Ag and Se upon Ag loading.\textsuperscript{4} It has been reported that CdSe NPs and aerogels can go through cation exchange with Ag$^+$ producing Ag$_2$Se nanostructures. However, this process requires efficient removal of Cd$^{2+}$ using coordinating solvents (such as methanol or ethanol). If such exchange occurs Ag-Se should appear in the PXRD pattern, which we have not observed in the present system. However, exchange of surface Cd with Ag is possible creating Cd-Ag-Se type bonding between particles.\textsuperscript{4} A change in binding energy was not noted between phase pure CdSe and CdSe/Ag hybrids indication the absence of $\alpha$-Ag$_2$Se and supporting the presence of a physical connection between CdSe and Ag NPs.\textsuperscript{4}
Figure 3.11. XPS spectra of CdSe aerogels: (A) Cd(3d_{5/2}), (B) Se(3d_{5/2}), (C) Ag(3d_{5/2}).
Figure 3.12. XPS spectra of CdSe/Ag aerogels: (A) Cd(3d<sub>5/2</sub>), (B) Se(3d<sub>5/2</sub>), (C) Ag(3d<sub>5/2</sub>).
**Table 3.2.** The volumes and nominal moles of CdSe, and Ag hollow NP sols used in the synthesis of CdSe/Ag aerogels along with the experimental molar ratio of CdS:Ag obtained from ICP-OES analysis.

<table>
<thead>
<tr>
<th>CdSe:Ag ratio</th>
<th>Volume of (0.04 M) CdSe Sol (mL)</th>
<th>Volume of (0.004 M) Ag sol (mL)</th>
<th>Nominal Moles of CdSe (x10^4) in the sol</th>
<th>Nominal Moles of Ag (x10^-7) in the sol</th>
<th>Experimental molar ratio of CdSe/Ag in aerogel (ICP-OES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSeNP/Ag 100/0</td>
<td>1.00</td>
<td>0.00</td>
<td>4.0</td>
<td>0.0</td>
<td>100/0</td>
</tr>
<tr>
<td>CdSeNP/Ag 100/0.2</td>
<td>1.00</td>
<td>0.20</td>
<td>4.0</td>
<td>8.0</td>
<td>100/0.76</td>
</tr>
<tr>
<td>CdSeNP/Ag 100/0.3</td>
<td>1.00</td>
<td>0.30</td>
<td>4.0</td>
<td>12.0</td>
<td>100/0.26</td>
</tr>
<tr>
<td>CdSeNP/Ag 100/0.5</td>
<td>1.00</td>
<td>0.50</td>
<td>4.0</td>
<td>20.0</td>
<td>100/0.09</td>
</tr>
<tr>
<td>CdSeNR/Ag 100/0</td>
<td>1.00</td>
<td>0.00</td>
<td>4.0</td>
<td>0.0</td>
<td>100/0</td>
</tr>
<tr>
<td>CdSeNR/Ag 100/0.2</td>
<td>1.00</td>
<td>0.20</td>
<td>4.0</td>
<td>8.0</td>
<td>100/0.12</td>
</tr>
<tr>
<td>CdSeNR/Ag 100/0.3</td>
<td>1.00</td>
<td>0.30</td>
<td>4.0</td>
<td>12.0</td>
<td>100/0.21</td>
</tr>
<tr>
<td>CdSeNR/Ag 100/0.5</td>
<td>1.00</td>
<td>0.50</td>
<td>4.0</td>
<td>20.0</td>
<td>100/0.37</td>
</tr>
<tr>
<td>CdSeNR/Ag 100/0.7</td>
<td>1.00</td>
<td>0.70</td>
<td>4.0</td>
<td>28.0</td>
<td>100/0.61</td>
</tr>
</tbody>
</table>
As described in the introduction chapter, the metal-semiconductor hybrid nanostructures hold important optical properties that have not been thoroughly investigated yet. To exploit the optical properties of CdSe/Ag hybrid aerogels and fundamental effects of plasmonic NP incorporation, CdSe/Ag hybrids were investigated utilizing steady-state and time-resolved absorption and emission spectroscopy.

The absorption across the valance and the conduction bands of spherical shaped CdSe and CdSe/Ag aerogels were studied by examining solid-state absorption spectra recorded at 300 K. The optical absorption was measured with low Ag loading from 0 - 1%. (Figure 3.13). The band edge absorption of phase pure CdSe was observed at 2.17 eV. At low levels of Ag loading of 0 - 1%, there was no significant changes in the band gap onset, which is consistent with previously reported studies for Ag NP loaded into CdSe. However band tailing effects were noted at 0.3% Ag incorporation. A slight systematic red shifting was observed with the increasing Ag content from 0 – 1% and quenching effects were seen with 0.7% or more Ag incorporation. Band tailing effects are expected to be an outcome of uneven distribution of Ag NPs within the CdSe network. However, the slight red shifting of absorption onset could be due to the overlap of the Ag Plasmon with the CdSe exciton. As the amount of Ag is increased above 0.7%, due to excessive loading of plasmonic metal NPs, the absorption properties gradually disappears due to higher direct electron tunneling between Ag and CdSe NPs.

The solid-state emission properties of aerogels were examined utilizing the PL spectroscopy at low temperature (5 K and 77 K). The emission spectra of spherical shaped CdSe, CdSe/Ag aerogels with 0.3%, 0.5%, 0.7% and 1% of Ag were recorded at 77 K (Figure 3.14). Band edge emission of CdSe aerogel was observed at 555 nm and
the trap state emission was observed at 710 nm. At 0.2% Ag loading a new emission maximum was observed at 640 nm and the previously observed band edge emission was significantly reduced. The new emission maximum is distinct from the band edge emission and the trap state emission of the phase pure CdSe aerogels obtained from CdSe NPs. At 0.5% Ag loading complete quenching of the band edge emission was noted and the predominant peak was only the new emission peak at 640 nm.

As the amount of Ag is further increased, the band edge emission decreases and a new emission peak at 640 nm increases possibly as a result of direct electron tunneling between CdSe and Ag NPs.\(^4\) This new hybrid emission is observed to be the most prevailing peak at 0.3% Ag loading and the band edge emission is significantly reduced with the increasing Ag concentration. The interactions between the metal and semiconductor NPs in the hybrids is supported by the existence of a new radiative relaxation pathway in sol-gel derived CdSe/Ag hybrid nanostructures.

A bandgap does not exist in metallic Ag. When metals are combined with semiconductors, the band gap of the semiconductor is reducing due to the overlap of conduction band of the metal with the bandgap of the semiconductor as the metal conduction band’s energy is intermediate of the valance and the conduction band of the semiconductor. As the amount of Ag increases, the flow of electrons increases and the energy gap of the semiconductor may reduce. Since metallic NPs do not contain any emission properties due to the overlap of conduction and valence band, with higher Ag loading the emission properties of the semiconductor NPs will be overtaken by the metals. This results in quenching of the band edge emission as well as the new hybrid emission at higher amount of plasmonic metal content.\(^80\)
**Figure 3.13.** Solid-state absorption spectra of CdSe NPs gels demonstrating the bandgap changes of the aerogels with increasing nominal Ag content 0 – 1%.

**Figure 3.14.** Solid-state PL emission spectra of spherical shaped CdSe and CdSe/Ag hybrid aerogels with 0, 0.2%, 0.5%, 0.7%, and 1% Ag loading at 77 K.
The absorption properties of rod shaped CdSe and CdSe/Ag aerogels with 0-25% Ag loading were studied by solid-state diffuse reflectance spectroscopy (Figure 3.15). The band gap of 1.94 eV was observed for phase pure CdSe aerogel and no significant changes were noted at low levels of Ag loading (0-1%) in the CdSe/Ag hybrid aerogels. However, systematic red shifting, band tailing, and quenching effects were noted with increasing Ag content from 1.2 – 25%. Typically, tailing effects are observed with uneven distribution of Ag hollow NPs in the CdSe gel framework. Bandgap quenching effects begins to appear with 5% Ag loading. However, at higher metal loading the bandgap continued to lessen and a complete depletion was observed at 25% Ag loading. This could be due to the position of metal electron cloud being in between the conduction and the valance bands of semiconductors. So, the dipole-dipole interactions increase. Thus, this reduction of the bandgap is attributed to higher dipole-dipole interactions among the metal and the semiconductor material.

The emission spectra of rod shaped CdSe with different Ag loading were recorded at 77K employing solid state photoluminescent spectroscopy (Figure 3.16). A sharp band edge emission of rod shaped CdSe aerogels were observed at 610 nm and the trap state emission was observed at 810 nm. Upon introduction of Ag hollow NPs, a new emission maximum is discerned at ~710 nm. The intensity of the band edge emission decreases with the increasing Ag loading in CdSe NR/Ag hollow NP hybrids. Interestingly, at 1% of Ag loading, the new hybrid emission peak is more prominent than the band edge emission, potentially due to the emergence of a new radiative decay pathways. The amount of Ag needed for changes in hybrid emission and the band edge emission peak were notably different in spherical shaped CdSe to that of rod shaped CdSe. This effect
could be attributed to the size of the CdSe NPs, where the spherical shape CdSe is ~4 nm, rod shape CdSe is ~17 nm long and ~4 nm wide compared to Ag hollow NP with a diameter of ~ 35 - 40 nm. Thus, smaller NPs are expected to make large number of interfacial linkages facilitating direct tunneling of electron from semiconductor to metal NPs. In comparison, such tunneling effects are expected to be limited in nanorods because of decreased surface area in rods compared to a dot, which may require higher amounts of Ag to establish similar number of interfacial linkages.

**Figure 3.15.** Solid-state absorption spectra of CdSe NRs demonstrating a red shift, quenching of bandgap and tailing effects with increasing Ag composition in the aerogels.
Figure 3.16. Solid-state PL emission spectra of rod shaped CdSe and CdSe/Ag hybrid aerogels with low to high (0 - 10%) Ag loading at 77 K.
TRPL spectroscopy was utilized to further understand the novel emission properties of CdSe/Ag aerogels. The biexponential decay times was examined for the band edge, emerging new emission maxima, and the trap state emissions of both spherical shaped and rod shaped CdSe/Ag hollow hybrids (Table 3.3). The aerogels produced from phase pure, spherical shaped CdSe NPs exhibit PL decay times of 1.83 ns at 555 nm (band-edge emission) and 1190 ns at 710 nm (emission from surface traps). In contrast, the hybrid aerogels produced from CdSe NPs and Ag hollow NPs exhibit a band-edge PL decay time of 1.38 ns, a trap state PL decay time of 944 ns, and interestingly a PL decay time of 685 ns for the new hybrid emission (640 nm), supporting the generation of novel radiative decay pathways.

On the contrary, phase pure CdSe aerogels produced from CdSe NRs exhibit a PL decay times of 3.02 ± 0.20 ns for the band edge emission (605 nm) and 984 ± 12 ns for the trap state emission (860 nm). In contrast, a decay time of 5.00 ± 0.24 ns, 1142 ± 66 ns, and 689 ± 20 ns was observed for the band edge, trap state, and new emission maxima in rod shaped CdSe/Ag hybrid aerogels. In both gel systems, the emerging new emission peak exhibited distinct PL decay times from those of the trap state and band-edge PL of phase pure CdSe counterparts, suggesting the creation of an alternate radiative decay pathway as a result of Ag loading into the CdSe gel network.
Table 3.3. The Decay Time and Amplitude Ratios from Biexponential Fits for All Emission Peaks of CdSe/Ag aerogels with Different Ag loading.

<table>
<thead>
<tr>
<th>Spherical Shaped CdSe/Ag Aerogels⁴</th>
<th>Ag % Composition</th>
<th>Band edge Emission (ns)</th>
<th>New Emission (ns)*</th>
<th>Trap State Emission (ns)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1.83 ± 0.03</td>
<td>-</td>
<td>1190 ± 120</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1.38 ± 0.05</td>
<td>685 ± 76</td>
<td>944 ± 50</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2.18 ± 0.06</td>
<td>596 ± 17</td>
<td>986 ± 83</td>
</tr>
</tbody>
</table>

*Multiple TRPL analysis are currently being performed for individual aerogel samples in collaboration with VCU Department of Electrical Engineering and the values will be updated accordingly.

<table>
<thead>
<tr>
<th>Rod Shaped CdSe/Ag Aerogels</th>
<th>Ag % Composition</th>
<th>Band edge Emission (ns)</th>
<th>New Emission (ns)</th>
<th>Trap State Emission (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>3.02 ± 0.20</td>
<td>-</td>
<td>984 ± 12</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>5.00 ± 0.24</td>
<td>689 ± 20</td>
<td>1142 ± 66</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.76 ± 0.13</td>
<td>631 ± 10</td>
<td>913 ± 18</td>
</tr>
</tbody>
</table>
CONCLUSIONS

In this research study, spherical and rod shaped CdSe particles were intermixed with Ag hollow NPs to produce hybrid systems composed of CdSe NP/Ag and CdSe NR/Ag aerogels. Co-gelation of metal and semiconductor NPs were achieved by progressively removal of thiolate surface functionality under ambient conditions. The use of non-oxygen transfer oxidant (C(NO₂)₄) creates low coordinated active sites on NP surface upon oxidative removal of surfactants. Consequently, these active sites undergo direct interfacial attachment to produce a “jelly-like” CdSe/Ag hybrid gel. Supercritical drying has been utilized to retain the porous morphology of the hydrogels and to produce robust metal-semiconductor nanoparticulate monoliths. The optimum physical connection of metal and semiconductor components in the hybrids resulted in novel/tunable photophysical properties that are vastly different from their individual counterparts.

Physical characterization of the hybrid aerogels revealed the existence of an interconnected network of hexagonal CdSe and cubic Ag NPs. The surface area analysis revealed the existence of a mesoporous superstructure and a systematic decrease with increasing Ag concentration owing to densification of the hydrogels. XPS studies suggested the presence of Cd²⁺ and Se²⁻ in CdSe aerogels. In addition, binding energy of reduced surface state of Se, Se_n²⁻ (54.3 eV), was detected which link individual NPs together into a fractal gel framework supporting the physical connection between NPs with no intervening ligands. Likewise, the binding energies of CdSe/Ag aerogels suggested similar characteristics to that of CdSe aerogels. It is anticipated that reduced
surface Se\textsuperscript{n−} species can also link Ag and CdSe NPs produce Ag-Se\textsuperscript{n−}Cd bridges in the hybrid gel framework.\textsuperscript{4}

The optical characterization of hybrid aerogels was carried out by employing diffuse reflectance, PL and TRPL spectroscopy. Solid state absorption spectra suggested a systematic red shifting of absorption onset and band tailing effects with increasing Ag concentration (0.2-1% for spherical CdSe/Ag hollows and from 0.5 – 25% for rod shaped CdSe/Ag hollow hybrid systems). Band gap quenching effects were observed with >1% Ag loading, owing to increasing metallic character. PL studies of the hybrid aerogels revealed a new emission maxima at 640 nm (spherical CdSe/Ag hollows) and 720 nm (rod shaped CdSe/Ag hollows) possibly due to a direct tunneling of photo excited electron and hole between the metal and semiconductor components in the hybrid systems. Thus, radiative recombination of the exciton from metal-semiconductor interface or Fermi levels of metallic Ag is expected to produce a novel radiative decay pathway. As a further proof, TRPL studies revealed decay times of 685 ns (spherical CdSe/Ag hollow NPs) and 689 ± 20 ns (rod shaped CdSe/Ag hollow NPs) for the hybrid emission, which are distinct from the band edge and trap state emission of phase pure CdSe NP and NR aerogels, supporting the generation of a novel hybrid emission.

Thus far, quenching of emission properties were reported with the incorporation of plasmonic metals into semiconductor NPs due to lack of control over interfacial interactions. PL quenching effects were reported in Ag surface modified CdS Quantum dots,\textsuperscript{80, 83} CdTe/Au hybrid aerogel produced via oxidation assembly,\textsuperscript{84} as well as many other core/shell metal-semiconductor (Au@CdS, Ag@CdS, etc.) hybrid systems.\textsuperscript{85-87} In this research study, we report the enhancement of optical properties by optimizing the
metal semiconductor interfacial interactions in low dimensional NP assembly. This new approach of co-gelation of CdSe and Ag NPs will likely have a major impact on the design and synthesis of high-efficiency light harvesting materials for future energy technologies.

Successful assembly of NPs in to a 3D network of chalcogenide aerogels while preserving the quantum confined optical properties of NPs allows the opportunity to develop these aerogels further for applications\(^{48}\). The physical properties of the CdSe/Ag aerogels, such as high surface area, mesoporosity, and interconnected network of NPs provide a great platform to develop efficient light harvesting systems and chemical sensor devices.\(^{48}\) It is reported that the diffusion of chemical species within a gel framework is almost equal to that of the air.\(^{88}\) Thus, rapid transport of molecules to/from pristine active surface is expected to facilities the sensing capability of NP–based aerogel materials.\(^{89}\)

Previously, the CdSe NPs were used with a hole-conducting polymer before applying in flexible photovoltaic devices.\(^{90}\) Unlike individual NPs, a continual flow of electrons is expected throughout the aerogel enabling such materials application in photovoltaics and other optoelectronic devices. Moreover, the tunability of individual components (\(i.e.\) desecrate metal and semiconductor NPs) allows the tuning of physiochemical properties of hybrids for desired applications. It is reported that the quantum confinement effects can be controlled by varying the density of chalcogenide aerogels, providing additional tools to engineer band structure.\(^{48}\) Thus, unique optoelectronic properties of spherical CdSe/Ag hollow NP and rod shaped CdSe/Ag hollow NP hybrids are promising for wide range of applications, specifically where optimum light-matter interactions are desired. Specific studies to test these premises are currently underway.
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EDUCATION

Master of Science, Inorganic Chemistry; May 2017 (expected)
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Thesis: “Efficient Integration of Plasmonic and Excitonic Properties of Metal and Semiconductor Nanostructures via Oxidation-Induced Self-Assembly.”

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HONORS/AWARDS AND SCHOLARSHIPS

Virginia Commonwealth University, Richmond VA
Honors College Scholarship
The National Society of Collegiate Scholar
Multicultural Academic Achievement Award
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Spring 2008
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Fall 2006
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RESEARCH AND TEACHING EXPERIENCE

Department of Chemistry, Virginia Commonwealth University, Richmond VA

Graduate Research Assistant  March 2016–Present
Advisor: Prof. Indika U. Arachchige

- Developed a general methodology for metal-semiconductor nanoparticle assembly into hybrid nanostructures via oxidation-induced self-assembly of colloidal nanoparticles.
- Studied the effects of morphology, composition, plasmonic and excitonic properties of metal semiconductor nanoparticles on successful generation of novel radiative decay pathways via steady state and ultrafast absorption and emission spectroscopy.
- Learned essential material characterization techniques including Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), Powder X-ray diffractometer (PXRD), Fluorimeter, UV-VIS Spectrophotometer.
- Learned nanomaterials synthetic technique including the use of Schlenk line, N₂ Glove Box, handling of air sensitive chemicals/materials and supercritical drying.

Department of Chemistry, Virginia Commonwealth University, Richmond VA

Teaching Assistant  Aug 2014 - Present
August 2007–December 2012

- Taught Chemistry 101 and 102 Recitation Class, Lead General Chemistry 101 and 102 labs
- Graded exams of undergraduate Biochemistry (CHEM403) lecture class, lab reports from general chemistry labs, exams and quizzes from general chemistry lecture classes.
- Provided feedback to undergraduate students on their exams, quizzes, lab reports, and other weekly written assignments and reports during office hours.
Department of Forensic Science, Virginia Commonwealth University, Richmond VA

Research Assistant August 2014–March 2016
Advisor: Prof. Christopher Ehrhardt

- Studied the DNA sequence of Yersinia pestis (Yp) grown in Lysogeny broth media to confirm species identity by DNA extraction followed by Polymer Chain Reaction (PCR) amplification with 42 mega Dalton virulent plasmid and examination through electrophoresis and DNA sequencing

- Learned the techniques of Bacterial spore preparation, DNA extraction and purification, PCR, Yp cell line maintenance, Electrophoresis, GCMS, and Optical Microscopy.

Department of Chemistry, Virginia Commonwealth University, Richmond VA

Graduate Research Assistant October 2011 - December 2012
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- Studied about the differential cellular accumulation and cytotoxicity of cis platin, TriplatinNC, BBR 3464, nucleolar targeting polynuclear platinum complexes on Chinese hamster ovary (CHO) cells.

- Learned the techniques of cell line maintenance, Glycosaminoglycan (GAG) Assay, 3-(4,5-Dimethylthiazol-2-Yl)-2,5-Diphenyltetrazolium Bromide (MTT) Assay and WST Cell Proliferation Assay, Cell synchronization, Flow cytometry, & intracellular Platinum accumulation by ICPMS

Department of Physiology and Biophysics, Virginia Commonwealth University, Richmond VA

Lab and Research Specialist I July 2010–January 2011
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- Studied distinct roles of hydrophobic residues on Hsp70 Inter-Domain Linker.

- Learned the techniques of SDS gel preparation, Quick change mutagenesis, Transformation, DNA Purification, PCR, Drop test, solution preparation for protein purification.
PUBLICATIONS


COMMUNITY OUTREACH AND VOLUNTEER SERVICES

*Kindle Institute, Richmond VA*
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United States ambassador for Sri Lanka  
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