The Pennsylvania State University

The Graduate School

DISCOVERY OF MATERIALS FOR RENEWABLE ENERGY APPLICATIONS

A Dissertation in

Chemistry

by

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ABSTRACT

The continuous development of new technologies has required the discovery of new materials with specifically tailored properties. Since the function of a material will be in part dictated by its structure, it is imperative that selective synthetic methods and protocols for materials characterization be established to enable materials with the desired structures and properties. In particular, a promising class of materials due to their sizedependent properties and tunable syntheses are nanoparticles. Nanomaterials are of interest for a variety of different applications including but not limited to; catalysis, optoelectronics, and biomedicine. While significant progress has been made towards understanding how to rationally control the kinetics and thermodynamics of synthetic processes, it can still be challenging to consistently obtain high-quality materials with the desired phase and morphology.

In this dissertation I highlight my efforts to discover, synthesize, and characterize materials that have applications towards renewable energy. I start by discussing two characterization techniques, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XRD is commonly used to evaluate the crystalline components in a material while XPS provides information about the elemental composition and chemical states at a material's surface. Key aspects that may be encountered when utilizing both techniques are highlighted for both bulk and nanomaterials. In regards towards XPS, several collaborations that I provided XPS data for are further discussed to highlight the diversity of information that the technique can provide.

Next, I describe efforts to synthesize and evaluate cobalt sulfide nanoparticles for their catalytic activity towards the electroreduction of CO₂ to value-added products. The polydisperse cobalt sulfide nanoparticles were synthesized through a colloidal approach and electrocatalytically tested on Ti foils. The observed gaseous and liquid products ranged from one-carbon to four-carbons, though all products had low Faradaic efficiencies. The cobalt sulfide particles were stable electrochemically for up to 24 hours at -0.49 V vs. RHE; however, it appeared that the particles were not structurally stable as the elemental composition post-testing indicated a severe loss of sulfur. Even though small amounts of products were generated, this result was important because it was the first report of a heterogeneous cobalt material that could promote C-C coupling towards C2-C4 products.

Finally, I discuss efforts to selectively synthesize three unique phases of cesium cadmium chloride nanoparticles; CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇. These nanoparticles were all made through similar approaches, though slight synthetic variations included reaction temperatures, injection rates of the cesium oleate precursor, and the starting amounts of the cadmium salt. The observed selectivity was hypothesized to arise from these variables working together to modulate the local concentration of cesium and cadmium ions available to react to form nanoparticles. The bandgaps of the three synthesized phases were evaluated experimentally using diffuse reflectance UV-Vis spectroscopy as well as computationally through DFT modeling done in collaboration with Prof. Ismaila Dabo's group. The large bandgaps (> 4.70 eV) that were predicted and observed places these phases into a category of materials known as ultra-wide bandgap semiconductors.

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Chapter 1

Discovery, Synthesis, and Characterization of Nanomaterials

1.1 Motivation

Since the onset of the digital age in 1970, great scientific advances have been made in fields such as electronics,¹ renewable energy,² and medicine.³ All of these advances, in addition to future advances, are driven by the discovery and characterization of new materials. The characteristic properties of a material will in part be dictated by its atomic arrangement and the material's morphology. It is therefore imperative to continually develop synthetic protocols that are scalable, sustainable, and allow for a wide variety of products that have distinct crystal lattices while additionally being able to control the shape and size of the material. While much of the pioneering discovery research has gone into bulk materials such as thin films and single crystals, the field of colloidal inorganic nanoparticles become a promising route to achieving the synthetic diversity needed to continue the advancement of new technologies.

1.2 Introduction to Nanomaterials and Their Properties

Compared to bulk systems, nanoparticles possess unique properties due to their small sizes. One of the most intriguing properties, especially for applications such as catalysis, relates to a nanoparticle's large surface area to volume ratio.^{4,5} This results in the energy at the surface to be much larger when the the nanoparticles are smaller. This is due to atoms at the surface being undercoordinated compared to atoms in the bulk of a material.

The destabilization of the surface of nanoparticles not only plays an important role for the active sites in catalysis but it can also significantly reduce the melting point of material. This is detailed by the Gibbs-Thomson equation and has been observed experimentally on Au and CdS particles by Koga and coworkers and Goldstein and coworkers, respectively.^{6–} ⁸ Finally, the small size of nanoparticles in combination with their curvature also impacts the strain at the surface. Simply put, smaller nanoparticles equate to more lattice strain.⁹ An increase in lattice strain is directly correlated with a materials hardness as demonstrated on different sized Au nanoparticles by Chianelli et. al.¹⁰



Figure 1.1: Variations in the band structure as particle size decreases from bulk to nano. Reproduced with permission from ref 11. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

In addition to the changes in the physical properties of a material when reduced to the nanoscale, the size-dependent properties of nanoparticles extend to a material's electronic and magnetic properties as well.⁴ Most notably, nanoparticles allow for the observation of effects due to quantum confinement which can only be realized when the dimensions of a nanoparticle are of a similar or smaller size than the Bohr exciton radius.^{11,12} Materials in this size regime are known as quantum dots.¹³ In a bulk material, the electronic states that comprise the valence and conduction bands are continuous as can be seen on the left in Figure 1.1. However, as the size moves from bulk towards the nanoscale, the energy levels become progressively more discrete.¹¹ This results in an inverse correlation between the size of the bandgap and the size of the particles, with small particles exhibiting larger bandgaps. The ability to easily alter a material's bandgap by controlling the particle size has significantly increased the interest for quantum dot semiconductors such as CdSe, CuInS₂, and cesium lead halide perovskites for a variety of applications such as photovoltaics, light emitting diodes, and medical imaging.^{14–20} The quantum confinement phenomenon is not only observed with small nanoparticles but can also be observed with thin layers of 2D materials such as MoS₂ or WS₂.²¹ Furthermore, 2D halide perovskites have also exhibited quantum confinement effects that are dependent on the number of perovskite octahedral layers.^{22,23}

The magnetism exhibited by metallic or metallic oxide nanoparticles is also sizedependent.⁴ As the nanoparticle size decreases to a critical diameter, the coercive force needed to demagnetize the material increases. Upon reaching the critical diameter, the required energy to overcome the coercive forces drastically decreases.²⁴ This is known as the single domain limit.²⁵ Continuing to decrease the particle size can result in nanoparticles that are superparamagnetic which means that slight thermal fluctuations can provide enough energy to flip the magnetic polarization.^{24–26} This phenomenon has been shown mainly for iron oxide-based materials such as the spinel, FeMn₂O₄ or γ -Fe₂O₃.^{27,28}

The size dependent properties discussed above highlight the diversity of applications that nanoparticles can be used for including catalysis, magnetism, and photoabsorbers. Unfortunately, the scope of materials that can be made as nanoparticles are limited when compared to bulk systems and the processes that govern their syntheses are not well understood.²⁹ While great advancements have been made in controlling the size, shape, and structure of nanomaterials, a deeper understanding is needed to ensure that they are applicable to large scale production and consumer ready applications.

1.2.1 Synthesis of Nanoparticles

Nanoparticle syntheses can be categorized into 2 general approaches. The first approach are top down syntheses which start from a bulk material and subsequently reduce the dimensions of the particles. Examples of these types of syntheses include ball milling,^{30,31} nanolithography,^{32,33} and hard templating.^{34,35} The second approach includes bottom up syntheses which start as the formation of seeds from molecular or atomic precursors and proceed through a nucleation and growth mechanism. Typical colloidal syntheses utilizing the bottom-up approach include hot injection,^{14,15} or hydrothermal methods.^{36–38} Comparing the two approaches, top down methods can produce a significantly larger quantity of nanoparticles and are typically more easily scaled than bottom-up syntheses. The most prominent advantage that bottom-up syntheses have over top-down methods however, relates to the fine control over the size, shape, and crystallinity of the synthesized nanoparticles.³⁹ Since the properties of nanoparticles are often dependent on their size and shape as discussed above, bottom-up methods, with the ability to synthesize monodisperse particles with specific dimensions in a variety of shapes, are often preferred.

In 1950, LaMer and coworkers proposed a synthetic mechanism that outlines the nucleation and growth of colloidal hydrosols.⁴⁰ In addition to the colloidal hydrosols that were initially reported, this mechanism has also been proposed as the predominant pathway for the growth of nanoparticles and can be seen in Figure 1.2.⁴¹ Briefly, the metal precursor, upon being exposed to the hot solution, either decomposes or is reduced to zero-valent atoms which will thus be the building blocks for the nanocrystal. As the reaction time



Figure 1.2: Mechanism of nanoparticle growth based on solution saturation. The monomer concentration is depicted as the black trace with respect to time. The three different stages are: (I) Formation of monomer species, (II) Formation of nuclei/seed particles, and (III) growth off the nuclei/seeds to form larger nanoparticles. Reproduced with permission from ref 41. Published by the Royal Society of Chemistry.

increases, the number of reduced atoms in solution will also steadily increase to the point of supersaturation at which time small nuclei are formed. Moving on from the nucleation event, the reaction enters the growth stage. The atoms present in solution begin to add layers onto the existing nuclei to form seeds. The formation of these seeds is vitally important because it is this step that dictates the structure and morphology of the resulting nanoparticle. This is due to the prohibitive energy penalties associated with the rearrangement of the nanoparticle seed past this point.⁴² It is accepted that during this phase, growth upon the surface of the nucleated seeds is more favorable than the nucleation of new seeds. It is important to remember that the growth of the nanoparticle is dynamic and that both the deposition of new atoms and the dissolution of atoms at the surface is happening simultaneously. The nanoparticles will continuously grow until an energy equilibrium is reached between the atoms on the surface which will favor dissolution and the atoms in the bulk which will favor growth. Additionally, this process will only occur if the solution remains oversaturated with the reduced atoms. Upon consuming the precursor monomers or reaching an energy equilibrium, the growth of the nanoparticles will terminate.⁴³

When discussing nanoparticle syntheses, it is important to highlight the differences between reactions run under kinetic vs. thermodynamic control. Products that are obtained under thermodynamic control will be the most stable or most energetically favorable. In terms of an energy landscape, the thermodynamically favorable product will be located at the global minima. Since there can also be local minima on this energy landscape, this implies that stability is relative and that a variety of end states, facets, and aspect ratios need to be considered before claiming thermodynamic control.⁴³ It can be challenging to alter the thermodynamics of a reaction; however, two common approaches are to change the reaction temperature or to change the ligand environment.^{42,43} Increasing the reaction temperature will increase the overall energy of the system allowing previously inaccessible activation barriers to be overcome. Ligands are important in nanoparticle chemistry as they can increase the colloidal stability and solubility in certain solvents.⁴⁴ More importantly, they can serve as capping agents for particular facets of a nanocrystal, prohibiting growth

in certain directions which induces anisotropic morphologies such as rods, platelets, or more exotic particles like dodecahedrons.^{45,46} From a thermodynamic point of view, this can alter the energy landscape to form a new global minimum or in essence, a new thermodynamically favored product.

Not only can ligands change the thermodynamic pathway of a reaction, but they can also influence the kinetics of a reaction. Kinetically favored reactions will travel along the pathway that has the lowest activation energy. This means that kinetically favored reactions can result in products that are higher in energy, or are metastable. Referring back to the energy landscape, this would mean that kinetically favored products are represented by local minima whereas the thermodynamic products were represented by the global minima. In general, it is easier to control the kinetics of a nanoparticle synthesis rather than control the thermodynamics.⁴³ Typical levers that can be adjusted for kinetic control include ligands, temperature, and injection rate of the precursor.^{42,43,47} As mentioned previously, ligands can alter both the thermodynamics as well as the kinetics of the reaction. The presence of ligands on the surface acts to inhibit the deposition and dissolution of atoms because in order for atoms to deposit onto or dissolve from the particle, the ligands on the surface would have to desorb.⁴³ This increases the energy barrier for growth and ultimately slows the rate of crystal growth. Similarly, altering the temperature and injection rate can lead to kinetically controlled products.⁴⁷ For example, one of the most common bottom-up methods for synthesizing nanoparticles is the hot injection method, where metal precursors are injected at elevated temperatures. This method was first presented by Murray and coworkers when making cadmium chalcogenide quantum dots.¹⁴ When cool precursor solution is injected into hot solvents, there is a swift drop in the reaction temperature. This decrease in temperature happens concurrently with the burst nucleation of seeds. The rapid formation of nuclei and drop in temperature slows the reaction rate during the growth stage allowing for the formation of monodisperse particles, thus placing the reaction under kinetic control.⁴³ Controlling both the kinetics and, to a certain extent, the thermodynamics of a reaction is thus vital to obtaining high quality, monodisperse nanoparticles.

1.2.2 Nanoparticle Characterization

While having fine control over a nanoparticle's size, shape, purity, and crystallinity is important, equally important is its characterization. There are numerous techniques that are available to researchers that can provide a wealth of information about a sample including its structure, elemental composition, optical properties, ligand coverage, etc. Due to the vast array of available characterization methods, it is vital to both understand a technique's limitations and ensure proper protocols are being followed during data collection and analysis to guarantee accuracy. Finally, it is good practice to consider materials characterization techniques as co-dependent meaning that many techniques are best used in combination with other techniques. Due to space limitations, the following brief discussion will only highlight the techniques that are utilized in this dissertation. For a further, more detailed discussion on materials characterization techniques, I would point readers to a review by Mourdikoudis and coworkers.⁴⁸

There are two types of electron microscopy that are commonly used to examine nanoparticles; transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM is based on a beam of high-energy electrons interacting with a sample, after

which some of the electrons will be transmitted while the others will be scattered. The transmitted electrons are then used to create a 2D image of the sample. TEM is highly dependent on the size, thickness, and composition of the sample as higher Z-elements will appear darker in a bright field image due to the increased absorption of electrons. On the other hand, SEM reconstructs a 3D image by collecting the scattered (compared to transmitted for TEM) electrons from a lower energy electron beam being rastered across a sample. TEM techniques have evolved such that samples can also be probed using a rastered beam as observed in SEM which is known as scanning transmission electron microscopy (S/TEM) and is most often used for Z-contrast imaging, energy dispersive Xray spectroscopy (EDS), and electron energy loss spectroscopy (EELS). The primary difference between SEM and TEM, and the difference most valuable when deciding what technique to use, is the spatial resolution. Due to the lower energy electrons and a larger field of view, SEM images have an approximate spatial limit of 1 nm. However, the spatial resolution of a TEM, particularly high resolution TEM (HRTEM), is approximately 20 times less at < 50 pm.

An elemental characterization technique that is commonly used in combination with SEM or S/TEM is energy dispersive X-ray spectroscopy (EDS). This technique maps the distribution of elements present in the nanoparticle sample. In short, the electron beam used for imaging can provide enough energy to eject a core electron past the Fermi level. The hole left by the ejected photoelectron is then filled by a valance electron which concomitantly releases an X-ray with an energy specific to the electronic transition for that particular element. Collecting these X-rays generates a spectrum which can then be depicted as elemental maps overlaid on the collected electron microscopy image. A limitation of EDS stems from the energy of the incident electron beam. The large energies, most commonly >10 keV, penetrate microns into the sample and so EDS characterization is not a surface sensitive technique. To obtain information about the elements present on the surface, a different technique like X-ray photoelectron spectroscopy (XPS) should be used. XPS is very similar to EDS; however, instead of measuring the X-rays generated from the relaxation of a valence electron, XPS measures the kinetic energy of the ejected photoelectron. The incident X-rays used in XPS are approximately 1.5 keV so the captured photoelectrons are typically generated within 3-10 nm of the surface. The measured kinetic energy of the photoelectron can then be converted to the binding energy for an electron of a particular element. This binding energy will shift based on the elements environment as well as chemical state making XPS a powerful technique to not only determine what elements are on the surface, but also to get a glimpse of its oxidation state and potential coordination with other elements. Finally, X-ray diffraction (XRD) is the most common method to probe the bulk structure of a nanoparticle. In principle, incident X-rays will constructively or destructively diffract off crystal planes in a material. Depending on the measured interference, a pattern is generated that is specific for each material based on its crystal structure and comprising elements. It is important to note that XRD will only give information about crystalline components in a material and is therefore best used alongside techniques like EDS to characterizes potential amorphous materials.

1.3 Nanoparticles for Catalytic Applications

Catalytic reactions are responsible for a large amount of the world's gross domestic product and play a pivotal role in the synthesis of manufactured chemicals.⁴⁹ For example,

the Haber-Bosch process which fixes N_2 to ammonia to be used in fertilizer accounts for 1% of the world's total energy usage.⁵⁰ Recently, catalytic reactions such as water splitting or CO₂ reduction have come to the forefront as research efforts focus on methods to sustainably produce renewable energy thereby mitigating negative environmental impacts from the consumption of fossil fuels.^{51,52} Nanoparticles, with the vast amount of morphologies and sizes that are readily synthesizable, present a rich platform to investigate structure-function relationships as they relate to catalysis.⁵³

The electroreduction or photoreduction of CO₂ has emerged in the past 5 years as a catalytic reaction of much importance given the steady rise in global atmospheric CO₂ concentrations.⁵² This increase in atmospheric CO₂ has negatively impacted human health and has led towards increases in both global temperatures and sea levels.^{54,55} Additionally, the reduction of CO₂ results in the formation of value-added products that could be used as chemical feedstocks or potentially as fuels. Catalysts for the electroreduction of CO₂ are generally zero valent metals such as copper, gold, and lead among many others.⁵⁶ Characteristic metrics used to evaluate a catalyst's activity for this reaction include the Faradaic efficiency of the obtained products, the onset potential where products are first observed, and the achieved total/partial current densities.⁵³ Catalysts that are able to catalyze C-C bonds are highly desirable; however, the only zero-valent metal that can achieve this is copper and this has become the "benchmark" catalyst in the field. Nanocrystals of copper have been made in a variety of different shapes including spheres, cubes, and nanowires, all exhibiting different product distributions.^{57–59} For example, Buonsanti et. al showed that cubic Cu nanoparticles with the thermodynamically preferred (100) facets showed an increase in faradaic efficiency for ethylene (41%) when compared

to polycrystalline Cu films.⁵⁸ Meanwhile, Li et al showed a completely different product profile when evaluating Cu nanowires which favored the formation of CH_{4} .⁵⁷ It was hypothesized that the preferential CH_{4} production was due to an increased density of edge sites due to crystal twinning. The size of nanoparticulate copper has also been explored in a report by Reske et al. They showed that as the size of the nanoparticles became smaller, the propensity to produce hydrocarbons became limited. Instead, CO and H₂ were shown to be the majority products for nanoparticles less than 15 nm.⁵⁴

Other metallic nanoparticles have also been studied, most notably that of gold. In a study by Kanan and coworkers, nanocrystals of Au containing large amounts of grain boundaries are more active for the reduction of CO2.⁶⁰ This result was rationalized by another report by the Kanan group which hypothesized that the activity increase could be due to either induced lattice strain which alters the initial binding activation energy of the CO₂ molecule or an increased number of active step sites on the gold surface.⁶¹ While there exists a large amount of literature evaluating the performance of monometallic and metallic alloys for the reduction of CO_2 , there has been significantly less studies exploring other materials such as chalcogenides. Interestingly, copper electrodes modified with chalcogens have shown to produce formate, a product not usually observed on polycrystalline copper foils.^{62,63} Therefore, the transition metal chalcogenide family is an interesting and promising space for the discovery of potential CO₂ reduction catalysts that may improve on the benchmark metrics set by copper electrodes. This is hypothesized because of the variety of accessible crystal structures and the large array of known synthetic processes that can finely control the nanoparticle's size and shape to optimize catalytic activity.

1.4 Experimental Work

In the following dissertation, I highlight my efforts to discover and synthesize a variety of different inorganic nanoparticles with potential applications towards catalysis and high-power electronics. I will also discuss two different characterization techniques that I had the opportunity to work with quite extensively during my pH.D. research, which resulted in multiple collaborations to help contribute key insights into different materials.

Chapter 2 expands on the discussion started in section 1.2.2, focusing specifically on two techniques, XRD and XPS. Firstly, the principles of XRD are covered in further detail. Furthermore, the effect of particle size and preferred orientation on the experimental patterns are discussed at length in reference to the wurtzite structure of CdS, as these two variables are commonly observed when collecting XRD patterns of nanoparticles. Finally, some key takeaways concerning careful data analysis are mentioned which include the difference between reference and simulated patterns, sample purity, and Vegard's law. This was published as an editorial in ACS Nano.⁶⁴ In addition to XRD, XPS is also discussed in chapter 2. This section briefly talks through the theory and instrumentation of XPS before spotlighting different methods of using the technique. These methods are presented through different collaborations I contributed to such as elemental analysis of materials before and after catalysis,⁶⁵ mechanistic investigations into the formation of complex heterostructured nanoparticles,⁶⁶ and depth profiling of bulk single crystals to obtain information about the depth of a passivating surface layer.⁶⁷

In chapter 3, cobalt sulfide nanoparticles are tested for the electroreduction of CO_2 to value added products. While copper is the benchmark catalyst for this reaction, its high overpotentials and low product selectivity leaves much room for improvement. Cobalt

sulfide, Co₉S₈, was chosen as an interesting catalytic target due to reports that chalcogenides can modify the activity of the transition metal to favor particular products as well as cobalt's ability to catalyze the reduction of CO₂ in molecular catalysts. Polydisperse Co₉S₈ nanoparticles were made colloidally through a one pot method. The particles were annealed onto Ti foils and were subsequently tested as CO₂ reduction catalysts in 0.1 M KHCO₃. The liquid products were analyzed by ¹H NMR and the gaseous products were analyzed through a collaboration with Caltech. Though the observed Faradaic efficiencies were poor (< 1%), the Co₉S₈ electrodes were able to produce up to C4 products. This result is encouraging because few heterogeneous catalysts, and none that contain cobalt, have been reported to make C3 or C4 products. This implies that further adjustments to Co₉S₈ catalyst, through addition of known catalytically active transition metals, could potentially result in increased product efficiencies.

Chapter 4 discusses the selective synthesis of three distinct phases of cadmium chloride nanoparticles, CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇. These particles were made through a hot injection method and the phase selectivity was hypothesized to arise from a myriad of three variables: 1) variations in starting amount of the metal precursors, 2) the reaction temperature, and 3) the injection rate of cesium oleate. These three variables working in concert allowed for control over the local Cs and Cd concentrations which in turn allowed for kinetic control to dominate during the growth of the nanoparticles. The bandgaps of the synthesized materials were determined both experimentally using diffuse reflectance UV-Vis spectroscopy and computationally through a DFT collaboration with Professor Ismaila Dabo and his group. It was determined that the materials possessed bandgaps that were all higher than 4.70 eV, which placed all three materials into a rare

category of ultra-wide bandgap semiconductors which are of interest for high-power electronics and deep UV lasing.

1.5 References

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Chapter 2

Discovery, Synthesis, and Characterization of Nanomaterials

2.1 Tutorial on Powder X-ray Diffraction for Characterizing Nanoscale Materials

2.1.1 General Considerations

Powder X-ray diffraction (XRD) is a common characterization technique for nanoscale materials. Analysis of a sample by powder XRD provides important information that is complementary to various microscopic and spectroscopic methods, such as phase identification, sample purity, crystallite size, and, in some cases, morphology. As a bulk technique, the information it provides can be correlated with microscopy data to test if microscopic observations on a small number of particles are representative of the majority of the sample. Despite its importance and ubiquity, the information contained in powder XRD data for nanoscale materials is not always fully harnessed, and in some cases, it is misinterpreted. This Editorial aims to provide the broad nanoscience and nanotechnology communities with a brief tutorial on some of the key aspects of powder XRD data that are often encountered when analyzing samples of nanoscale materials, with an emphasis on inorganic nanoparticles of various sizes, shapes, and dimensionalities. In this way, researchers across many fields, including those who are new to powder XRD or for whom it is not a mainstream technique, can be familiar with key diagnostic features and be better equipped to interpret them in the context of their samples. Readers who wish to learn about powder XRD in more depth and with greater rigor - including the theory, experimental setup, data acquisition protocols, and analysis - are referred to more comprehensive resources.¹⁻⁴

We consider CdS as a representative example, as it is a ubiquitous quantum dot material that is widely used in many nanoscience and nanotechnology fields. As nanoparticles, its band gap, and therefore also its color as well as other electronic and optical properties, is dependent upon the size and shape. The most stable crystal structure of CdS is wurtzite, which is shown in the inset to Figure 2.1. The XRD pattern for bulk CdS, simulated from crystallographic data,⁵ is shown in Figure 2.1. The first three peaks in the CdS XRD pattern correspond to the (100), (002), and (101) planes of CdS, and these are highlighted in the wurtzite crystal structure in the inset to Figure 2.1. The higher index planes are also labeled on the XRD pattern.



Figure 2.1: Simulated and indexed powder X-ray diffraction pattern for bulk $(1 \ \mu m)$ wurtzite CdS. The inset shows the crystal structure of wurtzite CdS with the (100), (002), and (101) planes highlighted.
When the crystallite size decreases from bulk to nanoscale dimensions, the XRD peaks broaden. The Scherrer equation (Equation 2.1),

$$D = \frac{\kappa\lambda}{\beta\cos\theta}$$
(2.1)

quantitatively describes the broadening of a peak at a particular diffraction angle (θ), as it relates the crystalline domain size (D) to the width of the peak at half of its height (β).⁶ The Scherrer constant, κ , is typically considered to be 0.9¹ but can vary with the morphology of the crystalline domains. The X-ray wavelength (λ) is a constant that depends on the type of X-rays used. Each peak can be evaluated independently and should produce a consistent crystalline domain size as long as the sample can be roughly approximated as uniform, spherical particles. Note that, in the Scherrer equation, the diffraction angle is in radians (not degrees) and corresponds to θ and not 2θ as is typically plotted in an XRD pattern. Also note that crystalline domain size does *not* necessarily correspond to particle size, as



Figure 2.2: Simulated powder X-ray diffraction patterns for wurtzite CdS spherical particles of different sizes that range from 1 μ m to 1 nm. The inset shows the 1, 2, and 5 nm XRD patterns on an expanded *y*-axis scale for clarity.

particles can be polycrystalline, containing multiple crystalline domains. When the crystalline domain size calculated by the Scherrer equation matches the average diameter

of particles determined by transmission electron microscopy (TEM) or other particle sizing methods, this observation suggests that the particles are single crystals rather than polycrystalline.

Figure 2.2 shows the same bulk XRD pattern for wurtzite CdS that was shown in Figure 2.1, along with XRD patterns for CdS having smaller crystalline domain sizes. As the size decreases from bulk (approximated as 1 μ m) to 50 nm, slight peak broadening is observed. It is difficult to calculate crystalline domain sizes using the Scherrer equation for particles in this size range, as most of the peak broadening is due to instrumental effects rather than particle size effects; careful analysis (*i.e.*, full profile fitting) is required to deconvolute these two independent contributors. Decreasing crystalline domain size from 50 to 25 nm causes more noticeable peak broadening. As crystalline domain size decreases further, peak broadening increases significantly. Below 10 nm, peak broadening is so significant that signal intensity is low and peaks overlap and can be difficult to discern. Particles having crystalline domain sizes below 5 nm become difficult to analyze, due to both broad peaks and low signal-to-noise ratios. Size-dependent XRD peak broadening has important implications for nanomaterial characterization. For example, if TEM analysis shows spherical particles having an average diameter of 10 nm, but the XRD pattern has sharp peaks that are more consistent with particles having much larger crystalline domain sizes, then the majority of the bulk sample is *not* composed of 10 nm particles; it is more likely that the microscopically observed 10 nm particles represent only a minority subpopulation.



Figure 2.3: Graphical representation of preferred orientation for nanoparticles having different shapes: (a) spheres, (b) cubes, and (c) rods. Simulated X-ray diffraction patterns for varying degrees of alignment (*i.e.*, preferred orientation) of wurtzite CdS particles along specific crystallographic directions: (d) [100], (e) [001], and (f) [110].

Not all nanoscale particles can be approximated by spheres, and powder XRD data can look different for particles of the same material that have different morphologies. The peak positions (*i.e.*, *x*-axis values) will remain the same, but the relative intensities of the peaks (*i.e.*, *y*-axis values) can change. For spherical particles, drying them to form a powder randomly orients them, and there is a statistically random distribution of crystal plane orientations with respect to the diffraction angle (Figure 2.3a). As a result, the relative intensities of all peaks are those expected based on the simulated diffraction pattern of the bulk powder, as shown in Figures 2.1 and 2.2. Note that peak broadening relates to the widths of the peaks, whereas the relative intensities relate to the height, so XRD patterns for spherical particles of nanoscale dimensions will have the same relative intensities as the bulk material, but the peaks will be broadened.

As particle shapes become nonspherical, there is a chance that, upon drying, they will orient in nonrandom directions. For example, a sample of cube-shaped particles dried or precipitated from solution will tend to orient with their flat faces parallel to the drying surface (Figure 2.3b). It is much less likely that nanocubes would dry with their corners or edges touching the drying surface, and therefore, the powder of nanocubes will be preferentially oriented in the crystallographic direction corresponding to the faces. Similarly, one-dimensional (1D) nanowires will tend to orient flat on a substrate upon drying (Figure 2.3c). Other particle shapes, such as octahedra or tetrahedra, may have different ways of orienting. The majority of the sample may exhibit preferred orientation, or only a fraction of it may, depending on the quality and size of the various particle shapes. In addition, the method in which the sample was dried to form a powder and/or how the XRD sample was prepared can influence the preferred orientation of the sample.

Figure 2.3d–f shows XRD patterns for wurtzite CdS corresponding to three distinct preferred orientation directions at various levels of alignment. First consider particles of CdS that are oriented along the [100] direction (Figure 2.3d). At the extreme limit, where all particles are aligned with their (100) faces parallel to the surface of the XRD sample holder, the only observable peaks will be those corresponding to the {h00} crystal planes that are parallel to (100), including (200), (400), etc. At intermediate levels of alignment, the intensities of the {h00} family of crystal planes will be enhanced relative to those of other planes [{*hkl*}, {*hk*0}, {00*l*}, *etc.*] because a larger-than- random fraction of particles is oriented in this direction.

Similar preferred orientation effects emerge for alignment in other crystallographic directions but with different relative peak intensities. For example, Figure 2.3e shows XRD

patterns for wurtzite CdS that exhibit preferred orientation along the [001] direction. Here, it is the {00*l*} peaks that are enhanced as the extent of alignment increases. Figure 2.3f shows XRD patterns corresponding to preferred orientation of wurtzite CdS along the [110] direction. Figure 2.3 highlights some of the ways in which preferred orientation can produce XRD patterns with different relative peak intensities than expected based on simulated or database patterns that correspond to crystallites oriented in a statistically random way, that is, bulk powders composed of nominally spherical particles. Likewise,



Figure 2.4: (a) Crystal structure of GeS and (b) transmission electron microscope image of GeS nanosheets. (c) Powder X-ray diffraction patterns showing significant preferred orientation in the [100] direction when GeS nanosheets are drop-cast (green) and only minimal preferred orientation when prepared as a powder (blue). Two simulated reference patterns, with (red) and without (black) preferred orientation, are shown for comparison. Adapted from ref 7. Copyright 2010 American Chemical Society.

XRD patterns for the same material, such as wurtzite CdS, can have a range of possible relative intensities depending on the direction and degree of alignment of particles in the XRD sample. The key to recognizing preferred orientation effects on relative peak intensities is to index the XRD pattern fully, that is, assign the (*hkl*) values to each peak and look for enhancements in the relative intensities of related families of planes, such as (110), (220), (330), *etc*.

To test if different relative intensities are due to preferred orientation effects, the same sample can sometimes be prepared for XRD analysis in ways that either minimize or maximize preferred orientation. For example, Figure 4 shows the crystal structure of GeS, along with a TEM image of GeS nanosheets.⁷ The corresponding XRD patterns in Figure 2.4 show experimental data for the GeS nanosheets drop-cast onto the XRD sample holder, which results in significant preferred orientation because the nanosheets tend to lie parallel to the surface of the sample holder. Figure 2.4 also shows experimental XRD data for the exact same GeS nanosheet sample that was first dried as a powder and mixed carefully to minimize preferred orientation. Simulated XRD patterns for bulk GeS (with no preferred orientation) and fully oriented GeS are also shown in Figure 2.4. The experimental XRD patterns are distinct, and comparison with the simulated XRD patterns indicates that the drop-cast sample shows almost full preferred orientation whereas the powder sample shows only partial preferred orientation. X-ray diffraction patterns of the same sample prepared in different ways should have different relative intensities, corresponding to enhancement of related families of planes. Such comparisons can help to validate claims that a bulk sample contains predominantly nanosheets (or other two-dimensional [2D] morphologies). Similar approaches can be applied to other morphologies, including 1D nanowires.



Figure 2.5: Simulated wurtzite CdS powder X-ray diffraction patterns of (bottom) 5 nm particles, (middle) 25 nm particles, and (top) a mixture that contains 75% 5 nm particles and 25% 25 nm particles.

Nanomaterial samples that include multiple distinct subpopulations of different sizes and/or shapes can produce more complex XRD patterns. For example, Figure 2.5 shows the simulated powder XRD pattern for a sample containing 75% 5 nm wurtzite CdS particles and 25% 25 nm wurtzite CdS particles. This bimodal particle size distribution produces peak shapes that contain narrower tips, from the contribution of the 25 nm particles having less peak broadening, and broader tails, from the contribution of the 5 nm particles having more peak broadening. As another example, consider nanoplates of wurtzite CoS that have average dimensions of 13 nm \times 5 nm and have the (001) plane as the base of the nanoplate (Figure 2.6).⁸



Figure 2.6: (a) Experimental and simulated powder XRD patterns for platelet-shaped wurtzite CoS nanoparticles. (b) High-resolution transmission electron microscope images of a CoS nanoplatelet viewed from the (left) side and (right) top. (c) Representation of the different effective thicknesses (*i.e.*, crystalline domain sizes) in different directions of the nanoplates, which correlate with different peak widths in the experimental XRD pattern. Adapted from ref 8. Copyright 2016 American Chemical Society.

Here, the crystalline domain size corresponding to the $\{00l\}$ peaks is 5 nm, so the (002) and related $\{00l\}$ peaks will have peak broadening that is consistent with a 5 nm crystallite. However, the crystalline domain size corresponding to the $\{h00\}$ peaks is 13 nm, so the (100) and related $\{h00\}$ peaks will have peak broadening that is consistent with a 13 nm crystallite. As a result, the (100) and (002) peaks, which are close to each other, have significantly different widths. The (101) peak has intermediate width, as it corresponds to a crystal plane that is oriented diagonally along the particle (Figure 2.6). The differences in peak broadening for different families of planes are consistent with the dimensions and crystal orientation that are observed microscopically, which reconciles the microscopic and bulk data to confirm that the nanoplate morphology comprises the majority of the sample. Note that, in the wurtzite CoS case, preferred orientation in the XRD pattern was purposely minimized by preparing the sample by a method that did not allow the nanoplates to align extensively.

Finally, consider a mixture of different crystalline forms of CdS. Although CdS prefers to crystallize in the hexagonal wurtzite structure, the cubic zinc blende polymorph is also known⁹ and can be present in samples. Figure 2.7 shows simulated XRD patterns for wurtzite CdS and zinc blende CdS, along with a 1:1 mixture of the wurtzite and zinc blende phases, both as 20 nm spherical particles. The zinc blende peaks overlap with some of the wurtzite peaks, so the XRD pattern of the mixture appears to have higher relative intensities, relative to wurtzite, for the peaks to which the zinc blende phase contributes. Figure 2.7 also shows the XRD pattern for a sample containing 20 nm nanoplates of wurtzite CdS that have 35% preferred orientation in the [001] direction. It is important to note that these two XRD patterns - a mixture of zinc blende and wurtzite CdS and pure wurtzite CdS with partial preferred orientation along the [001] direction - appear very similar. The first three peaks are almost identical in relative intensity, and subtle features differentiate the two, including the presence or absence of a few low-intensity peaks (*i.e.*, a peak near 31°) and the relative intensities of some of the higher-angle peaks. Careful

analysis is therefore required to differentiate scenarios that can lead to similar XRD patterns.



Figure 2.7: Simulated powder X-ray diffraction patterns for 20 nm particles of wurtzite and zinc blende CdS. A simulated pattern for a 1:1 mixture of wurtzite and zinc blende CdS is also shown, along with wurtzite CdS that has 35% preferred oriented in the [001] direction.

Nanosheets, which are ubiquitous in 2D materials research, present an extreme case of both crystalline domain size and preferred orientation effects. Consider an atomically thin nanosheet that has lateral dimensions on the order of 100 nm. The crystalline domain size in all directions of the nanosheet, except for the crystal plane that it contains, will be on the order of, and sometimes smaller than, 1 nm. As can be seen in the XRD patterns in Figure 2.2, peaks for such small crystalline domain sizes are so broad that they are not observable. If such thin nanosheets are precipitated, they will almost assuredly exhibit significant preferred orientation such that they will stack vertically but in a random way. To visualize this, consider a deck of cards. If a deck of cards is thrown up in the air and the cards are allowed to settle on the floor, they will be stacked vertically on top of each other, but they will be misaligned and in random orientations laterally. A similar scenario occurs

when exfoliated nanosheets are restacked, either through precipitation or deposition on a surface. Applied to XRD of nanosheets, the effective crystalline domain size is small and the system contains significant disorder. Thin nanosheets are often buckled when restacked as a powder, and their stacking periodicity has disorder due to this buckling. Diffraction peaks arising from stacked nanosheets therefore will not be sharp, and the most intense diffraction peaks (for samples exhibiting significant preferred orientation) will correspond to the average distance between nanosheets. For atomically thin nanosheets that are allowed to precipitate in analogy to how cards restack, the XRD pattern will simply be a series of broad {00*l*} peaks. For thicker and more rigid nanosheets, like the GeS system shown in Figure 2.4, the stacking can become more uniform and the nanosheets can be sufficiently thick to show XRD patterns that can look more like nanoplates with preferred orientation. However, it is worth noting that restacking of exfoliated nanosheets is *unlikely* to yield a precipitate that exactly matches that expected for the bulk material from which it was derived. The nanosheets are unlikely to stack with perfect vertical and lateral alignment - such an achievement would be quite notable! Therefore, the XRD pattern for exfoliated and restacked nanosheets, if they comprise the majority of the sample, should not match that of the bulk material.

Given the considerations outlined above, it is notable that XRD patterns for samples of nanoparticles having different sizes and shapes can look different, and careful analysis of the XRD data can provide useful information and also help correlate microscopic observations with the bulk sample. Electron diffraction patterns, which can be acquired during TEM analysis, can be compared with XRD patterns of the bulk sample to confirm that the particles being imaged are those that comprise the majority of the sample. There are also other considerations to keep in mind when analyzing powder XRD data that are especially relevant for nanoscale materials.

2.1.2 Phase Identification

One application of powder XRD is phase identification, which is often accomplished by comparing an experimental XRD pattern with a reference pattern that is either simulated or obtained from a database. In such cases, an unambiguous and complete match between the experimental and reference patterns is needed. Arbitrary peaks predicted by a reference pattern cannot be missing in the experimental XRD data without justification. All peaks in the reference pattern, which includes both of their diffraction angles and intensities, should be accounted for in the experimental pattern unless there is a clear and justified rationale for why certain peaks may be missing or have different intensities, such as preferred orientation, as discussed above. To accomplish this comparison, experimental XRD patterns having sufficient signal-to-noise ratios are needed so that low-intensity peaks can be observed.

Phase identification by XRD for some systems, especially nanoscale materials, can be particularly challenging because of nearly indistinguishable diffraction patterns. For example, Au and Ag are both face-centered cubic metals that have sufficiently similar lattice constants that Au and Ag nanoparticles (which have broadened peaks) cannot be differentiated by XRD. Similarly, the XRD patterns of two forms of iron oxide, magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃), are sufficiently similar that, for nanoparticles with broad peaks, they cannot be distinguished by XRD. Differentiating the hexagonal close-packed form of elemental nickel from hexagonal nickel carbides (Ni₃C) and nitrides (Ni₃N) can be similarly challenging. In these and other cases, additional characterization techniques are important for achieving phase identification.

2.1.3 X-ray Diffraction Databases vs Simulated Reference Patterns

Reference XRD patterns can be obtained from several sources. Commercially available powder diffraction databases are excellent resources of broad scope that are often available with the software used to analyze experimental XRD data. When reference patterns from such databases are used to compare with experimental data, the specific reference file identification number should be given, as there are often multiple entries for the same phase. It is also worth noting that relative peak intensities of database patterns can sometimes differ from those observed experimentally. For example, database patterns based on older crystallographic data could include semiquantitative peak intensities (*i.e.*, very strong, strong, medium, weak, very weak, *etc.*), which were determined by rough quantitation of diffraction lines on films that were used prior to the availability of digital detectors.

Powder XRD patterns can also be simulated directly from crystallographic data, and software programs that can do this often are also capable of including preferred orientation and peak broadening due to nanoscale crystalline domains. In these cases, it is important to cite the reference from which the crystallographic data were obtained. It is also important to make sure that all crystallographic data have been entered into the simulation program correctly. Errors in data entry - including obvious errors such as typos in fractional coordinates and less obvious errors such as omission of fractional site occupancies and use of nonstandard space group settings - can lead to errors in the simulated patterns. Crystallographic information files (CIFs) can also be downloaded and used to simulate XRD patterns, thereby avoiding manual data entry. Here, it is important to understand the source of the CIF and its reliability and/or feasibility. For example, journals that include CIFs as part of the Supporting Information for manuscripts often require CIF checks prior to acceptance, thereby helping to ensure that they are reasonable. Crystallographic information files generated from computationally derived databases are also useful, but it is important to know if the CIF files correspond to known, stable phases that have been experimentally validated or if they correspond to previously unknown and/or metastable phases that are unlikely to be the products of routine syntheses and, therefore, would require additional characterization and justification to confirm that they formed.

2.1.4 Amorphous vs Nanocrystalline Products

X-ray diffraction is a powerful characterization tool for identifying crystalline phases in a sample, but one important limitation involves amorphous components that lack long-range crystallographic order, as they do not produce diffraction patterns with discernible peaks. An XRD pattern for a sample that contains a significant impurity of an amorphous component, in addition to one or more nanoscopic crystalline components, may look indistinguishable from a similar sample containing only the nanocrystalline component(s). Additional characterization is therefore needed to test sample purity and/or to determine whether or not some of the sample is amorphous. It is worth noting that XRD patterns for amorphous phases can appear similar to those observed for nanoparticles having diameters that are less than 2 nm; both would exhibit similar, significant peak broadening.

2.1.5 Sample Purity

As noted above, sample purity determination can require several characterization tools. Along these lines, it is also important to consider the limits of detection and quantification of typical laboratory X-ray diffractometers, which can be on the order of 5–10%. These are just approximate values, and they can vary significantly depending on the instrument and the sample being characterized. Samples that produce XRD patterns having low signal-to-noise ratios, including poorly crystalline materials and nanoscale materials having significantly broadened peaks, can contain large amounts of components that do not produce XRD peaks that rise significantly above the background noise. Low intensity peaks, which may correspond to impurities, can also be difficult to observe. The presence of asymmetric peaks may be due to stacking faults and other defects or a distribution of compositions in compounds that could be present as alloys or solid solutions.

2.1.6 Lattice Constraints

For highly crystalline bulk materials with high signal-to-noise ratios and sharp peaks, lattice constants (in units of Å) are often reported to three or four decimal places, with the uncertainty (error) corresponding to the last decimal place. To obtain such precise values, profile fitting and refinement are required. For nanocrystalline materials, which have lower signal-to-noise ratios and broad peaks, such precision in lattice constants is difficult to achieve. Reported lattice constants are therefore not expected to contain three or four decimal places unless rigorous and reliable profile fitting and refinement were carried out (and even then, such precision may not be possible). To identify trends in lattice constants across multiple related samples, such as alloys of systematically varying compositions, it is sometimes necessary to include an internal standard in the samples for calibration purposes. For example, by including small amounts of a bulk crystalline compound such as LaB₆ in samples of alloy nanoparticles (assuming that the LaB₆ peaks do not overlap significantly with those from the nanoparticles), the XRD patterns of the alloy nanoparticles can be compared more accurately by applying a zero-point shift so that the LaB₆ peaks all overlap. (A zero-point shift involves minor shifting of the *x*-axis, for legitimate reasons caused by errors such as sample height alignment, that is achieved by adding or subtracting a very small constant value.) In this way, any changes in the peak positions arising from the sample can be considered reliable because they change relative to those of the internal standard, which remain fixed.

2.1.7 Vegard's Law

Changes in composition can change the properties of many types of nanoscale materials. For example, Au–Ag alloy nanoparticles have a surface plasmon resonance energy that depends on the relative amounts of Au and Ag alloyed in the nanoparticle. Likewise, the emission energy (color) of semiconductor quantum dots can tuned by composition, that is, by substituting some of the Cd or S in CdS nanoparticles with Zn or Se, respectively. Powder XRD data for such solid–solution nanoparticles typically reveal lattice constants that are intermediate between the end members. Vegard's law is the

empirical observation that there is often a linear relationship between the lattice constants (and in some cases properties) of an alloy and its composition.¹ For example, Vegard's law would predict that the lattice constant for a Au_{0.5}Cu_{0.5} alloy would be the average of the lattice constants of Au and Cu. Because of this relationship, XRD is often used to determine composition, and composition is used to predict lattice constants. It is important to remember that Vegard's law is not a law but rather an empirical relationship that often has deviations. It is useful as a rough estimate, but it has limitations. Therefore, it is best used in conjunction with other characterization techniques that can accurately measure composition.

2.1.8 Conclusions

Powder XRD provides useful information about structure, phase, composition, shape, size, crystallinity, and other important features of nanoscale materials, although unambiguous sample characterization almost always requires complementary experimental and/or computational methods. Powder XRD data for nanoscale materials can often be straightforward to analyze for the key information that is needed, but other times, it can be quite complex. This tutorial highlighted several key features of XRD patterns that are often encountered in nanoscale materials as well as diagnostic insights that we hope will be helpful in interpreting data. However, the selected topics were by no means exhaustive nor did the discussions capture all aspects of data collection and analysis, including subtle (but important) nuances that require full-profile fitting and refinement to identify, to quantify, and to deconvolute. In the end, it is important to recognize the capabilities and limitations of powder XRD for nanoscale materials when collecting and analyzing data as well as to ensure that claims based on XRD data are accurate, appropriate, and not overreaching.

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2.1.9 References

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2.2 X-ray Photoelectron Spectroscopy

2.2.1 Introduction to X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a powerful surface characterization technique that can be used for a wide array of materials including bulk powders, thin films, and nanoparticles. The XPS process, along with Auger spectroscopy, were coined electron spectroscopy for chemical analysis (ESCA) and was originally reported by Kai Seigbahn in 1967.¹ XPS primarily provides information about the elemental composition of a sample's surface, typically ranging from 3-10 nm. Additionally, XPS can provide details on local interactions between elements from which bonding information can be extracted. This data can afford insights into material formation mechanisms and indicate species that are relevant to applications such as electrocatalysis.²

XPS is based on the photoelectric effect which states that electrons can be ejected from a material upon being irradiated with electromagnetic radiation as long as the incoming radiation has sufficient energy to overcome the electron's binding energy. XPS uses X-rays as the electromagnetic radiation and the technique directly measures the kinetic energy of the ejected photoelectron. The measured kinetic energy can be converted to the binding energy of the ejected electron through equation 2.1³

$$B.E. = h\nu - K.E. - \Phi_s \tag{2.1}$$

where B.E. is the binding energy of the electron, hv is the incident X-ray energy, K.E. is the measured kinetic energy of the ejected photoelectron, and Φ_s is the work function of the material. Typically, Φ_s is offset by a determined instrumental correction factor and is therefore considered constant. The most common radiation sources are Mg or Al anodes due to their narrow line widths, which provide for increased spectral resolution. The Mg or Al anodes produce K α X-rays at energies of 1253.6 eV or 1486.6 eV, respectively.³ It is important to note that the incident photons generated by the anode can travel up to micrometers into the sample, exciting and ejecting photoelectrons "deep" within the bulk. However, only the electrons at the sample's surface will be ejected without losing energy from elastic collisions with other electrons. The kinetic energy of these surface photoelectrons is what appears as peaks in the obtained XPS spectrum.





Figure 2.8: Schematic showing the incident X-rays ejecting a core photoelectron above the Fermi level of the material. Each distinct energy level of a particular element will have a specific binding energy allowing for a spectrum to be obtained indicating what elements are present at the surface of a sample.

The XPS process is highlighted in Figure 2.8. Incident X-rays of known energy irradiate a sample's surface. Upon overcoming the binding energy and the work function

of the material, a photoelectron is ejected. This photoelectron is ejected past the Fermi level and its kinetic energy can then be measured. The kinetic energy of the ejected photoelectron will depend on the element, quantum number, and orbital from which the electron was ejected.^{2,3} The XPS process is very similar to other elemental characterization techniques such as energy dispersive X-ray spectroscopy (EDS) or Auger spectroscopy with slight differences. The EDS process is outside the scope of this chapter; however, the Auger process can occur concomitantly with the photoelectron process as explained briefly below. In the Auger process, much like in the photoelectron process, the incident radiation will eject a core photoelectron. The main difference for the Auger process stems from the ejection of a second photoelectron that simultaneously coincides with the relaxation of a valence electron into the hole left by the first ejected photoelectron. These secondary photoelectrons are known as Auger electrons. For this reason, it is common to observe Auger electron peaks while conducting XPS experiments. It is crucial to remember that Auger electrons are not dependent on the incident radiation energy. It is because of this that the peak positions will not change on a binding energy axis, but instead will shift based on their measured kinetic energy.^{2–4}

2.2.3 X-ray Photoelectron Spectrometer

The XPS instrument is highlighted briefly in Figure 2.9. Monochromatic X-rays are generated from the X-ray source (1 in Figure 2.9). Two ion guns are used to charge compensate at the sample's surface. First, an electron gun is used to neutralize the build-up of positive charge caused from the ejection of electrons during analysis and second, an Ar^+ ion gun is used to help further balance any negative charging effects for the electron

neutralizing gun. The ejected photoelectrons then move through an aperture with multiple lenses (2 in Figure 2.9) that are used to both focus the photoelectrons as well as retard their energy before hitting the analyzer. Once through the aperture and its lenses, the photoelectrons travel through a hemispherical concentric analyzer (3 in Figure 2.9). The



Figure 2.9: Typical schematic of an XPS instrument. The anode (1) provides the incident X-rays which generate the photoelectrons. The photoelectrons are focused and their kinetic energy is retarded through the aperture/lens (2). The analyzer (3) generates an electric field which disperses the photoelectrons by kinetic energy before hitting the detector (4).

analyzer is composed of two electrically charged plates that generate an electrostatic field. This field bends the photoelectrons towards a detector (4 in Figure 2.9) and a spectra is then generated. The photoelectrons that strike the middle of the detector after moving through the analyzer are known to have an energy defined as E_0 , the pass energy. Photoelectrons that have kinetic energy *greater* than E_0 will hit the detector closer to the outer plate while photoelectrons that have kinetic energy *smaller* than E_0 will strike the detector closer the inner plate (Figure 2.10). The pass energy is crucial in determining the resolution of the scan, with lower pass energies resulting in higher resolutions and higher pass energies resulting in lower resolutions. However, the disadvantage to using lower pass

energies is a marked decrease in the observed signal-to-noise ratio. This means that longer acquisition times may be needed to obtain quantifiable spectra at lower pass energies.^{2,5}



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Figure 2.10: Schematic showing the photoelectron flight paths based on their kinetic energy. Photoelectrons that have a higher kinetic energy (purple) will travel farther than photoelectrons with less kinetic energy (red).

2.2.4 General Considerations

As stated above, each element has specific electron binding energies that are well tabulated.³ Typically, larger principal and azimuthal quantum numbers result in lower observed binding energies since these electrons are located farther from the nucleus. Small deviations from these tabulated values indicate a change in the atom's local electronic environment. A shift towards lower binding energies indicates that atom is more reduced while a shift towards higher binding energies indicates that the atom is more oxidized. This can be easily rationalized through the concepts of ionization energy and electron shielding. For instance, the required ionization energy needed to remove an electron from M^0 to M^+

is much less than the energy needed remove an electron from M⁺ to M²⁺. Additionally, outer electrons will be shielded from the charge of the nucleus resulting in lower ionization energies. Slight deviations in the peak positions can also stem from bonding elements being more electronegative or electron withdrawing. The induced partial charges will result in the peaks shifting towards higher binding energies for partially positive elements and towards lower binding energies for partially negative elements. Peak shifts are thus extremely important in XPS as they provide crucial information about a material's surface electronic structure.^{2,3}

When conducting XPS experiments, there are some important concepts to remember before starting sample analysis. There are two different types of scans that should be run for each sample: a survey scan which will provide a general overview of the elements present and high-resolution scans of the elemental regions of interest. Firstly, in order to reduce the convolutedness of obtained spectra, it is important to ensure that the regions chosen for high-resolution scans do not overlap. Deconvolution of overlapping regions can be especially challenging and if not careful, may inaccurately represent the measured sample's elemental ratios. Therefore, analyzing the survey scan for overlapping or unexpected elemental regions prior to assigning high-resolution regions is a must. Secondly, collected spectra need to be calibrated to a set energy value with the most commonly used calibration point being the C 1s peak. This originated from Siegbahn's initial XPS report where adventitious carbon from pump oil was used as the reference as its presence on the surface steadily increased over time. It should be noted however, that XPS calibration should be carefully considered. Recently, a viewpoint published by Hultman et. al outlined challenges with solely using adventitious carbon as the calibration

point.⁶ The criticisms against using the C1s peak as a calibration point ranged from a report claiming adventitious carbon can catalytically react on the surface of a material to another report stating that the binding energy changes based on the amount of carbon adsorbed on the surface.^{7,8} Ultimately, the unknown source and variable composition of the adventitious carbon present on a material's surface calls into question whether using the C1s peak is a reliable means of calibration. Unfortunately, there is no perfect solution to circumvent this problem though some potential solutions that were proposed include noble metal decoration or assessing chemical states based on the Auger parameter.^{9,10} For the noble metal deposition method, the difference in binding energy between noble metals deposited onto a surface and the binding energy of the corresponding bulk noble metal would more accurately give the magnitude of charge on the surface.⁹ Similarly, the Auger parameter method would take the difference between the kinetic energy of the Auger line and the photoelectron line. This would result in a value that is independent of static charge and would be unique to each material.¹⁰ Finally, shifts in the photoelectron lines, which would indicate oxidation state changes, for certain elements can be difficult to observe. Such elements include, but are not limited to, silver and copper. In these situations, it is best to collect both the photoelectron lines as well as the corresponding Auger line as this can result in a more accurate analysis of an element's oxidation state.

The last part of this chapter will discuss three different studies where XPS was used to provide key insights into experimental processes. The first study examines AgRh nanoparticles with XPS before and after catalysis to determine the material's stability under operating conditions. The second study investigates the formation mechanism of Pt-Cu3PdN heterostructured nanoparticles, in particular using XPS to determine when nitrogen was incorporated into the nanoparticles. Finally, XPS depth profiling is used to determine the identity and thickness of a passivating layer preventing further etching from Mo₂AlB₂ single crystals. These studies are meant to highlight some unique ways in which XPS can be used to examine nanoparticles as well as highlight the key data obtained for each study through this technique.

2.2.5 XPS Analysis of AgRh Nanoparticles for the Electrochemical Hydrogen Evolution in Acidic Media



Figure 2.11: High-resolution XPS spectra of the Rh 3d and Ag 3d regions for AgRh alloy nanoparticles, both pre (a,b) and post (c,d) chronopotentiometry experiments. Peak deconvolutions show metallic rhodium (red), metallic silver (red), and oxidized rhodium (blue). Adapted from ref. 11. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

In its simplest form, XPS is able to provide information concerning both the elemental composition and chemical states at a material's surface. This information can be valuable for comparing a material before and after catalytic testing. For example, bulkimmiscible AgRh alloys were made as nanoparticles and tested for the hydrogen evolution reaction (HER).¹¹ In this collaboration with Albert Darling, I was able to use XPS to examine the nanoparticles pre and post catalysis which was helpful to investigate the material's stability after operation under an applied potential. The obtained spectra can be seen in Figure 2.11. The nanoparticles before catalysis showed the presence of metallic Rh (Figure 2.11a, red shading), metallic Ag (Figure 2.11b), as well as a RhO_x species (Figure 2.11a, blue shading). It can be seen that the RhO_x peaks are shifted to the left, or towards higher binding energies, which is consistent with a more oxidized Rh species. The elemental ratio between metallic Ag and metallic Rh was approximately 1:1 which agreed well other characterization techniques such as EDS and XRD. The post-catalysis XPS spectra showed a drastic decrease for the contribution of RhO_x (Figure 2.11c, blue shading) decreasing from a pre-catalysis metal to metal oxide ratio of 80:20 to a post-catalysis ratio of 96:4. Meanwhile, the ratio between metallic Rh (Figure 2.11c, red shading) and metallic Ag (Figure 2.11d) remained approximately 1:1, showing that alloying was maintained. The obtained spectra provided key information about the stability of alloy at the nanoparticles surface during catalytic testing for the HER in acidic conditions. Since the most significant change in the surface composition of the AgRh particles was the reduction of a native RhO_x species, it was concluded that the alloying between Ag and Rh was stable throughout the catalytic HER testing process.

2.2.6 Insights into Complex Heterostructure Formation Using XPS

XPS can also be used to study the formation mechanisms of materials by examining aliquots of reaction mixtures to determine the time points at which certain elements are observed. In particular, XPS can be especially useful for quantitative analysis of lighter elements such as nitrogen when compared to a similar elemental analysis technique such as EDS. For the case of nitrogen, this is because nitrogen has a low absorption cross section



Figure 2.12: High-resolution XPS spectra of the N 1s region for the Pt-Cu₃PdN heterostructures. The samples were collected after reacting at 170 °C for 10 (top) and 15 minutes (bottom). The red contribution is due to the nitrogen in the Cu₃PdN structure while the blue contribution is from the oleylamine nitrogen. Reprinted with permission from ref. 12. Copyright 2019 American Chemical Society.

and its X-ray line is approximately 0.4 keV. This means the Be window in the EDS detector absorbs a majority of the nitrogen X-rays which significantly lowers the signal to noise and subsequently convolutes quantitative analysis. One particular collaboration that I was involved in with Robert Lord was using XPS to examine when nitrogen was incorporated into Pt-Cu₃PdN heterostructures.¹² Briefly, Pt nanoparticles were used as seeds to nucleate the growth of Cu₃PdN. It was observed by HRTEM/EDS that the Cu initially formed a thin shell around the Pt nanocubes. This was then followed by the deposition of Pd on the high surface energy corners of the Pt nanocubes with the concomitant coalescence of Cu. The incorporation of nitrogen was monitored by XPS at 5-minute time intervals throughout the 15-minute reaction. At 10 minutes, the XPS spectra showed a broad peak in the N 1s region indicating that two different species were present (Figure 2.12). At 15 minutes, the spectra showed a profile that could be deconvoluted into two peaks (Figure 2.12). The peak centered at 397 eV was assigned to the nitrogen in the Cu₃PdN lattice. This peak in particular was shown to significantly increase from 10 to 15 minutes which agrees with the formation of Cu₃PdN at the corners of the Pt seed. The peak centered at 399.5 eV was assigned to the nitrogen in the oleylamine and as expected, did not change significantly from 10 to 15 minutes. In addition to collecting the N spectra, spectra of the Cu and Pd



Figure 2.13: High resolution XPS spectra of the Pt 4f, Cu 2p, and Pd 3d regions of the synthesized Pt-Cu₃PdN heterostructures. Samples were collected after reacting at 170 °C for 10 minutes (top row) and 15 minutes (bottom row). Adapted with permission from ref 12. Copyright 2019 American Chemical Society.

regions were also obtained as shown in Figure 2.13. The spectral positions of the Cu $2p_{3/2}$ and the Pd $3d_{5/2}$ peaks at 932.7 eV and 335.4 eV, respectively, agree well with the known literature values for Cu-N and Pd-N interactions. The XPS data collected for this study was instrumental in helping to confirm at what time point the nitrogen was incorporated into the nucleated Cu₃PdN. This allowed for important insights to be drawn concerning the formation of these complex heterostructures and for comparisons to be drawn between other hybrid dimer systems such as Fe₃O₄ on Pt. These results could point towards a controllable lever to synthesize new hybrid nanoparticles in the future.

2.2.7 XPS Depth Profiling on Modified Mo₂AlB₂ Crystals

While XPS can probe up to the first 10 nanometers of a material's surface, information about the elemental composition deeper within the bulk of a material can be obtained through depth profiling. Depth profiling is accomplished through a sputtering process where ions bombard a surface, removing materials upon impact. One of the more commonly used sputtering ions is Ar^+ . Depth profiles can be particularly helpful to determine the thickness of a passivating layer on a material's surface. As an example, I used XPS depth profiling in a collaboration with Lucas Alameda to examine passivating layers of AlO_x on MoAlB single crystals.¹³ MoAlB has a layered crystal structure composed of Al atoms interleaving two-dimensional sheets of MoB. With a rise in interest concerning 2D materials and their intriguing properties, MoAlB is an attractive target to potentially achieve 2D MoB through the selective removal of Al atoms. The removal of Al atoms occurred through subsequent alkaline etching and heat treatments, yielding a Mo₂AlB₂ intermediate. EDS characterization showed the presence of Al on the surface,

which indicated that the Al had indeed been removed from the crystal structure. However, the removal of Al was theorized to form a passivating aluminum oxide layer which was preventing further Al removal. To determine the thickness of the AlOx layer, depth profiling was used and the spectra can be seen in Figure 2.14. Ion sputtering removed approximately 3 nm of material and was performed between each of the 15 scans. It was observed that an increase in milling depth was accompanied with an increase in signal for Mo and B and a concomitant decrease in signal for oxygen. The decrease in oxygen signal implied that the oxide layer was sputtered away, specifically between scans 1 and 2, while the increase in Mo and B signals upon milling confirmed the underlying Mo₂AlB₂ crystal.



Figure 2.14: High resolution XPS spectra of $Mo_2AlB_2-AlO_x$ corresponding to the Mo 3d, Al 2p, O 1s and B 1s regions. Scan 1 shows the $Mo_2AlB_2-AlO_x$ crystals before heat treatment. Each subsequent scan milled 3 nm of material and scans 5, 10 and 15 are shown for each region. The arrow indicates the intensity change due to milling. Reprinted with permission from ref 13. Copyright 2019 American Chemical Society

Corroborating this data was the Al spectra which showed that overall intensity did not change with sputtering; however, the Al peaks shifted towards lower binding energies, signifying the presence of a more reduced Al species. This is expected in the Mo₂AlB₂ structure because the Mo-Al bonds have been predicted to be metallic indicating an approximate zero-valent chemical state.¹⁴ From the EDS and XPS depth profiling experiments, it was concluded that the passivating layer on the surface of the Mo₂AlB₂ intermediate was an AlO_x material that was approximately 1 to 3 nm thick.

2.2.8 Concluding Remarks

XPS is a versatile surface characterization technique that gives information about the elemental and chemical states at the surface of a material, usually within the first 3-10 nm. XPS's versatility stems from its ability to characterize a variety of materials including nanoparticles, bulk single crystals, or powder samples. The data analysis guidelines and examples discussed previously are meant to provide the reader with a clear understanding of what type of data XPS can provide and how the technique can be a powerful tool in obtaining insights into materials synthesis, guiding further experimentation based on the byproducts seen on the surface, or examining a materials stability against corrosion after catalytic testing.

2.2.9 References

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Chapter 3

Cobalt Sulfide Nanoparticles for the Electroreduction of CO₂

3.1 Introduction

The dependence on non-renewable energy sources such as fossil fuels and the resulting increase in atmospheric concentrations of CO_2 due to their combustion has negatively impacted the environment through climate change and is also a concern to human health.^{1,2} It is therefore critical to develop methods to reduce the amount of atmospheric CO_2 through methods such as renewable energy alternatives or to convert CO_2 into value added products for chemical synthesis or fuels. Particularly, the electrochemical reduction of CO_2 is a promising method to synthesize value added products, allowing for a reduced global carbon footprint in addition to providing a platform to couple emerging renewable energy technologies.^{2–4}

The overall electroreduction of CO_2 to value-added products is composed of two half reactions; the cathodic reaction where CO_2 is reduced and the anodic reaction where water is oxidized to oxygen, or the oxygen evolution reaction (OER). The cathodic and anodic half reactions, along with the overall reaction, can be seen in equations 4.1, 4.2, and 4.3, respectively.³

$$xCO_2 + nH^+ + ne^- = Product + yH_2O$$
(4.1)

$$H_2 0 = 0_2 + nH^+ + ne^-$$
(4.2)

 $xCO_2 + yH_2O = Product + zO_2$ (4.3)

The equilibrium potentials (vs. RHE) of the cathodic half reactions often are slightly positive; however, due to the large difference between the equilibrium potentials of the cathodic reaction and the anodic OER, the actual potential needed to drive the overall reaction is usually greater than 1 V. Additionally, both the OER and the reduction of CO_2 require large overpotentials which further increases the potential required for this reaction.³ While the electroreduction of CO_2 is a promising platform to reduce CO_2 concentrations, the process is currently inhibited by high overpotentials (mentioned above), sluggish kinetics due to the large number of electrons needed for more reduced products, poor product selectivity, and competition against the more favorable hydrogen evolution reaction (HER) being in aqueous electrolytes.^{3,5–7} Catalysts for the reduction of CO₂ are dominated by zero-valent transition metals such as Ag, Sn, Cu, and Au.^{8,9} Of the transition metals, copper is the benchmark catalyst due to its ability to produce products containing 2 or more carbons (C2+), albeit at high overpotentials and with low selectivity.⁸⁻¹⁰ Recently, efforts to improve on copper's metrics have focused on changing the electronic environment by evaluating materials such as alloys or oxides. For example, alloys such as AuCu, AgCu, and Ni_xGa_y, have all improved either the faradaic efficiencies (FE) or reduced the overpotentials needed to produce particular products when compared to pure Cu.¹¹⁻¹³ Additionally, oxide derived Cu catalysts have been shown to suppress the formation of CH₄ and increase the production of C₂H₄.^{14–16} The increased activity for C2 products on oxide derived Cu has been theorized to emerge from an increased density of grain boundaries as well as larger electrochemical surface areas from the rapid removal of oxygen while under reducing potentials.^{14,15}

While both alloys and oxides have received significant attention, transition metal sulfides have been less prevalent in the CO_2 reduction literature. Transition metal sulfides can adopt a large range of crystal structures and coordination environments since sulfur is able to bond with both metals as well as itself, forming a polysulfide anion.⁷ The rich diversity of coordination environments found within the transition metal sulfide family suggests a possibility for a multitude of different active site reactivities that could enable



Figure 3.1: Pentlandite structure of Co_9S_8 . The yellow spheres are sulfur atoms while the blue atoms/polyhedra are tetrahedrally coordinated cobalt and the red sphere/polyhedron is octahedrally coordinated cobalt.

the formation of particular products. While most reduced products that are observed after testing a copper metal catalyst such as methane, ethylene, or ethane are widely accepted to go through an adsorbed carbon monoxide species (*CO), it has been reported that adatoms of sulfur or other chalcogens on a copper surface could alter this pathway to instead produce formate.^{17–19} A recent study indeed demonstrated this, reporting the production of formate with a FE of 80% over a sulfur-modified Cu catalyst.²⁰ Other sulfide catalysts including the transition metal dichalcogenide MoS₂ have also been reported to form
products including 1-propanol with FE's of 2-5% on single crystal terraces.²¹ The promising results from the transition metal sulfide catalysts above suggests that a deeper investigation of other transition metal sulfide catalysts may yield new catalysts for the electroreduction of CO_2 .

Much like other transition metal sulfides, cobalt sulfide can adopt compositions as well as crystal structures including the pentlandite structure, Co_9S_8 . This structure can be seen in Figure 3.1 where cobalt occupies two distinct sites leading to octahedral (red polyhedra) and tetrahedral (blue polyhedra) coordination with sulfur. Briefly, catalysts containing cobalt are underrepresented in the CO_2 reduction literature. In fact, to the best of our knowledge, heterogeneous cobalt catalysts for the electroreduction of CO₂ have only been reported a handful of times and has otherwise been used as a dopant for other heterogeneous materials.^{22–27} In one study, CoS₂ nanocubes were reported as electrocatalysts that reduced CO₂ to CO with 80% FE.²⁸ The propensity to catalyze the reduction of CO₂ versus protons to form hydrogen was hypothesized to arise from the large number of S planes, which are predicted to suppress the hydrogen evolution reaction when compared to S edges.²⁸⁻³⁰ While cobalt materials have not been extensively studied as heterogeneous CO₂ reduction catalysts, cobalt has seen traction as molecular CO₂ reduction catalysts, particularly with cobalt phthalocyanine complexes.^{31–34} Therefore, the study of a cobalt sulfide material is intriguing because it couples sulfides with a transition metal whose potential has not been thoroughly explored for CO₂ reduction. Co₉S₈ has shown promise as a bifunctional material that has been investigated for use in metal-air batteries in addition to being evaluated as a catalyst for the HER.^{35–38} While the HER is a parasitic side reaction to CO_2 reduction, the activity of Co_9S_8 for this reaction is far worse than the



Figure 3.2: Co_9S_8 structure and the planes of S atoms (yellow) when the structure is viewed parallel to the (111) plane which is shown in red for reference.

benchmark HER catalyst, Pt. For instance, Co_9S_8 nanoparticles tested in neutral media exhibited overpotentials of approximately 340 mV to reach -10 mA/cm² whereas Pt requires approximately 50 mV of overpotential to reach the same current density.^{39,40} When carbon-armored Co_9S_8 nanoparticles were evaluated for the HER in neutral media, the required overpotential to reach -10 mA/cm² was 280 mV which was slightly less than what was needed for pristine Co_9S_8 particles.³⁹

The HER activity of Co_9S_8 is slightly worse compared to other prominent cobalt sulfide catalysts such as CoS_2 that have been tested in neutral pH. For example, CoS_2 has been shown to require approximately 225 mV to reach similar current densities for the HER.⁴¹ Additionally, Co_9S_8 has been reported as an active catalyst for the for other reactions such as the ORR as well as the reduction of N₂ to ammonia.^{42–44} Finally, it was mentioned previously that the HER could be suppressed by increasing the amount of S planes relative to S edges.²⁸ As shown in Figure 3.2, the Co₉S₈ structure has planes of S atoms (yellow) when viewing the structure parallel to the {111} family of planes. This implied that nanoparticles exhibiting preferred orientation along the [111] direction could potentially show activity for the reduction of CO_2 . It was because of this that Co_9S_8 was chosen as an interesting catalytic target for the electroreduction of CO_2 .

We herein demonstrate the synthesis of Co_9S_8 nanoparticles and their performance as a catalyst for the electroreduction of CO_2 . The nanoparticles were made through a colloidal reaction involving a cobalt(II) reagent with 1-dodecanethiol at elevated temperatures. The polydisperse nanoparticles were deposited onto Ti foil and annealed before their activity for CO_2 reduction was evaluated in 0.1 M KHCO₃. While Co_9S_8 nanoparticles exhibit low FE's, we show that they are capable of producing C1 to C4 products. Even though low FE's are reported, this result is still significant since non-copper materials do not typically catalyze the production of C2+ products. This is also the first report to our knowledge of a heterogeneous cobalt catalyst that shows activity for CO_2 reduction. Therefore, this family of cobalt materials presents a favorable platform to expand upon non-copper containing catalysts that can reduce CO_2 to C2+ products.

3.2 Experimental Section

3.2.1 Materials

Cobalt(II) chloride (CoCl₂, 97%), oleylamine (70%, technical grade), 1dodecanethiol (98%), trioctylphosphine (97%), and titanium foil (99.7%, 0.127 mm) were purchased from Sigma-Aldrich. Potassium bicarbonate (99%) and N,Ndimethylformamide (DMF) were purchased from Alfa Aesar. Flash-Dry Silver colloidal suspension paint was purchased from SPI supplies and two-part epoxy [Loctite, Hysol 9460] was purchased from Grainger. Nanopure water (18 M Ω) was obtained from a Barnstead Nanopure Analytical Ultrapure system. Solvents (hexanes and isopropyl alcohol) were of analytical grade. All chemicals were used without further purification.

3.2.2 Synthesis of Co₉S₈

Cobalt sulfide nanoparticles were synthesized by slightly modifying a previously reported synthesis.⁴⁵ CoCl₂ (110 mg, 0.85 mmol) and trioctylphosphine (10 mL) were added to a 3-neck, 100-mL round bottom flask with a condenser, thermometer adapter, alcohol thermometer, magnetic stir bar, and rubber septum. After the cobalt salt dissolved, 1-dodecanethiol (10 mL) and oleylamine (5 mL) were then added causing the solution to become a red-brown color. The flask was cycled 3 times between Ar and vacuum to ensure an oxygen-free environment. The solution was quickly heated to 250 °C under a static argon atmosphere for 10 minutes. The reaction was then quenched using a room temperature water bath. The solution was transferred to centrifuge tubes and the nanoparticles were isolated by centrifugation at 13,500 rpm for 3 minutes. The red supernatant was discarded and the black precipitate was resuspended in 1:1 mixture of hexanes and isopropyl alcohol. This washing procedure was repeated twice more. The washed product was stored in hexanes for further characterization and catalytic testing. It is important that no solvent or anti-solvent be added during the first centrifugation step as doing so will result in the formation of a red gelatinous substance from which the nanoparticles *cannot* be isolated.

3.2.3 Electrode Preparation

The procedure to prepare working electrodes is similar to the previously reported methods, with slight modifications. Co_9S_8 nanoparticles were dropcast onto approximately 0.25 cm² pieces of Ti foil until a uniform and opaque film was observed. After a 2-hour treatment at 400 °C under a constant flow of inert gas (UHP Ar), the foils were then attached to a copper wire using colloidal silver paint. A two-part epoxy was then used to ensure that no silver paint or copper wire was exposed to the solution as well as to electrically insulate all surfaces other than the Co_9S_8 catalyst deposited onto the Ti foil.

3.2.4 Electrochemical Measurements

Electrochemical measurements were attained using a Gamry Reference 600 potentiostat. Measurements were conducted in a 2-compartment H-cell that was separated by a Nafion 117 membrane (fuelcellstore.com) to prevent cross-contamination from the working electrode to the counter electrode. The electrolyte used in all experiments was 0.1 M KHCO₃ (pH 6.8) while the counter and reference electrodes were a Pt wire and Ag/AgCl, respectively. To ensure there were no leaks in the system, all ground joints were greased or tightly fitting septa were used. CO₂ was bubbled through the solution for 20 minutes prior to the start of catalysis. All electrochemical measurements, linear sweep voltammograms and chronoamperometry scans, used the current interrupt method to correct for the iR drop due to uncompensated resistance and the polarization data were collected at 10 mV/s. All reported voltages are normalized against the RHE unless

otherwise stated. Headspace and solution sampling occurred at the end of a chronoamperometry scan. The solution aliquots were analyzed using ¹H NMR while the headspace samples were analyzed using gas chromatography.

3.2.5 Product Characterization

A 1 mL aliquot of the headspace was acquired at the end of the chronoamperometry scan and analyzed using gas chromatography/mass spectrometry (Agilent) in the Prof. Lewis' lab at Caltech with collaborator, Dr. Carlos Read. Single point calibrations were conducted using analytical gas standards purchased from Air Liquide with the balance being Ar. Liquid products were characterized through ¹H NMR (Bruker AVIII-HD-500) using a water suppression package which used a RF-pulse to saturate the signal at 4.8 ppm which corresponds to water. ¹H NMR samples were prepared by taking a 2 mL aliquot of the solution post-electrolysis and adding DMF (0.1 μ L) as an internal standard. A small volume of the DMF containing solution (500 μ L) was then added to D₂O (200 μ L) and well mixed through vortexing before being transferred to a NMR tube for analysis. Each sample was analyzed for 256 scans to ensure enough analyte signal.

3.2.6 Materials Characterization

Powder X-ray diffraction (XRD) was collected on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) and a PANalytical Empyrean diffractometer using Cu K α radiation ($\lambda = 1.5406$ Å) with a PIXcel^{3D} detector. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) with energy dispersive spectroscopy (STEM-EDS) images were collected on a FEI Talos F200X

S/TEM at an accelerating voltage of 200 kV. STEM-EDS maps were analyzed using the Bruker ESPIRIT 2 software. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) maps were collected on a FEI Nova NanoSEM 630 FESEM. Images were collected at an accelerating voltage of 3 keV and a working distance of 2-3 mm while maps were collected at 10 keV and a working distance of 5 mm. For EDS mapping, the K α_1 lines were used for both Co (6.92 keV) and S (2.31 keV).

3.3 Results and Discussion

Colloidal cobalt sulfide (Co₉S₈) nanoparticles were synthesized using a modified literature procedure.⁴⁵ The HAADF-STEM image shown in Figure 3.3a depicts a polydisperse sample of nanoparticles with sizes ranging from 10 to 110 nm. Additionally, the particles exhibit a variety of different shapes including prisms, rhombuses, triangles, and truncated polyhedra. The wide variety of shapes that can be seen in Figure 3.3a could arise from different pathways. The first pathway could be simply due to Ostwald ripening, or the coalescence of smaller particles into larger particles. The larger prism-like particles could be composed of agglomerations of the smaller truncated polyhedra or triangles which are also observed in the HAADF-STEM image (Figure 3.3a). The second pathway could be due to the ligands used during the synthesis, oleylamine and trioctylpohsphine. These long chain organic molecules could potentially bind to a specific facet, inhibiting growth in that crystallographic direction. The latter hypothesis is further strengthened by the evidence of preferred orientation in the XRD pattern shown in Figure 3.3e. The experimental Co₉S₈ pattern matches well with the simulated reference pattern; however,



Figure 3.3: (a) HAADF-TEM image showing polydisperse Co_9S_8 nanoparticles. (b-d) STEM-EDS maps showing the colocalization of S and Co on the synthesized particles. (e) Experimental and simulated XRD pattern for Co_9S_8 .



Figure 3.4: (a) Magnified and (b) zoomed-out SEM images of Co_9S_8 nanoparticles annealed onto a Ti foil. (c,d) SEM-EDS maps showing the colocalization of S and Co on the nanoparticle film deposited on Ti foils. (e) Experimental and simulated XRD pattern for the Co_9S_8 on Ti foil where Ti is denoted by the *.

the peaks corresponding to the {111} family of planes in the experimental pattern are overexpressed compared to the reference pattern suggesting preferred orientation in the [111] direction. Additionally, the relatively sharp peaks in the XRD pattern indicate an average particle size that is large which corresponds well with the HAADF-STEM images. The STEM-EDS maps in Figure 3.3b-d show that cobalt and sulfur are evenly distributed throughout the particles and there are no localized regions of any particular element.

In order to evaluate Co_9S_8 performance as a catalyst for the electroreduction of CO_2 , the nanoparticles were dropcast onto Ti foil and annealed under a flowing stream of UHP Ar. Figure 3.4a-c show a zoomed-out SEM image and SEM-EDS maps of an annealed foil. The SEM-EDS maps indicate the presence of both cobalt and sulfur after the thermal treatment in the expected ratio of 9 to 8, respectively. Figure 3.4d shows a magnified SEM image of the annealed film. After the heat treatment, the nanoparticles have appeared to lose the distinct morphologies as was observed in Figure 1a. Instead, the SEM image in Figure 3.4d shows a morphology resembling grains of rice that are approximately 150-200 nm in length. The loss of the distinct nanoparticle morphologies is also observed through XRD as shown in Figure 3.4e. The {111} family of planes is no longer overexpressed compared to the reference pattern. Rather, the experimental peaks of the annealed Co_9S_8 film match the simulated reference pattern in terms of both peak position and expected intensity. The asterisks in the XRD pattern depict the peaks corresponding to the Ti foil substrate.



Figure 3.5: Polarization data of the Co_9S_8/Ti electrode tested in 0.1 KHCO₃ that had been purged with CO_2 (black) Ar (red) for 30 minutes prior to electrocatalysis.

Electrodes were fabricated by attaching the annealed Co_9S_8 /Ti foils to a copper wire using colloidal silver paint. The entire ensemble was coated in a two-part epoxy, except for the Co_9S_8 nanoparticle film, to ensure that all parts were electrically insulated from the solution. Linear sweep voltammograms (LSVs) were conducted at a sweep rate of 10 mV/s after purging the solution, 0.1 M KHCO₃, with either Ar or CO₂ for 20 minutes (Figure 3.5). After purging the electrolyte with Ar, the acquired LSV showed a small feature around -0.4 V and achieved a relatively low current density. Based on the known literature values of electrochemical redox events for cobalt, the small feature would most likely be the reduction of a $Co(OH)_2$ species on the surface of the electrode, the presence of which is unsurprising given the aqueous electrolyte. Comparatively, when the electrolyte was purged with CO₂, a significant increase in current density was observed in addition to the disappearance of the redox feature at approximately -0.4 V. The large increase in current density observed for an electrolyte purged with CO₂ compared to an electrolyte purged with Ar suggested that the Co₉S₈ catalyst was active for the electroreduction of CO₂.



Figure 3.6: Galvanostatic trace of a Co_9S_8/Ti electrode held at -0.49 V vs. RHE for 24 hours.

Figure 3.6 shows a representative chronoamperometry scan collected at -0.49 V for a Co₉S₈/Ti electrode. All chronoamperometry scans were allowed to go for 24 hours after which, liquid and gaseous headspace aliquots were taken to determine the analyte concentrations. The chronoamperometry scan shows a minimal decrease in the current density over the course of 24 hours indicating that the material was stable under applied potentials. The gaseous aliquot was taken and analyzed using gas chromatography and mass spectrometry (GC/MS) through a collaboration with Dr. Carlos Read and Dr. Nate Lewis at Caltech. The resulting spectrum is shown in Figure 3.7. Peaks for methane, ethylene, ethane, propane, propene, and butane were observed, albeit in very low quantities. Methane has the largest faradaic efficiency at 0.38%. The major C2 gaseous products are ethylene and ethane, with faradaic efficiencies of 0.11% and 0.13%, respectively. Finally, further reduced products including C3 and C4 products are also



Figure 3.7: Representative GC/MS spectra collected by Dr. Carlos Read at Caltech showing the gaseous products observed from the Co_9S_8 electrode at -0.49 V vs. RHE. The blue trace is the standard calibration gasses and the black spectrum is the experimental spectrum.

Product	Faradaic Efficiency (%)		
Methane	0.38		
Ethylene	0.11		
Ethane	0.13		
Propane	0.02		
Propene	0.02		
Butane	0.01		
Total	0.66		

Table 3.1: Gaseous products and their corresponding FE's measured by GC/MS

observed in extremely small quantities. The faradaic efficiencies for the gaseous products are summarized in Table 3.1. The remaining balance is composed of both CO₂ and H₂.

The liquid products were characterized using ¹H NMR, of which a representative spectrum is shown in Figure 3.8. The aliquots were taken after a 24-hour chronoamperometry scan at -0.59 V. A water suppression package was used to mitigate the large peak associated with the water protons at 4.8 ppm. This allowed for characterization of analytes with lower concentrations. In order for quantitative measurements, N,N-DMF

was used as an internal standard because its proton peaks did not interfere with any peaks corresponding to potential analytes. The products that were observed by ¹H NMR were predominately carbonyl containing compounds such as acetate and formate. Additionally,



Figure 3.8: Representative ¹H NMR spectrum of an electrolyte aliquot taken after testing a Co_9S_8/Ti electrode for 24 hours at -0.49 V vs. RHE. A water suppression package was used to suppress the water signal at 4.7 ppm. The DMF standard peaks are at 2.75, 2.90, and 7.82 ppm.



Figure 3.9: (a) Faradaic efficiencies for alcohols produced by a Co9S8/Ti electrode over a range of different applied potentials. (b) Faradaic efficiencies for formate and acetate produced by a Co9S8/Ti electrode over a range of different applied potentials.

small amounts of alcohols including including methanol, ethanol, and butanol were also observed. The faradaic efficiencies for these products over a range of potentials can be seen in Figure 3.9. For acetate and formate, the amount of detected product generally decreases as the potential becomes more negative. However, at the most negative potential of -0.59 V, the calculated faradaic efficiency for both formate and acetate increased. This increase in efficiency could be due to competing product formation processes becoming less favorable at lower applied potentials. Meanwhile, the formation of methanol and ethanol was observed to increase as the potential became more negative. The turn-on potential for methanol was -0.39 V while the turn-on potential for ethanol was 200 mV lower at -0.59 V. Finally, the formation of t-butanol was also observed by ¹H NMR. The maximum amount of butanol produced was observed at -0.29 V. As the potential was lowered, the amount of butanol produced significantly decreased, eventually stopping at an applied potential of -0.6 V.

Even though the Co₉S₈ nanoparticles exhibit low faradaic efficiencies for a variety of products, C3 and C4 products were still produced in quantities that are above the detection limits of the GC/MS and the ¹H NMR. The formation of C4 products is particularly encouraging because to our knowledge, C4 products have only been observed on copper-based catalysts. On the other hand, C3 products have been made by a variety of different catalysts that include but are not limited to copper-based catalysts, NiGa and NiA1 alloys, and MoS₂ single crystals or bulk films. While the Co₉S₈ nanoparticles will require extensive catalytic optimization to increase the reported faradaic efficiencies reported herein, the propensity that the material shows for the production of value-added products is intriguing and should be further explored.

The formation of CO is widely accepted as the crucial intermediate to achieving C2+ products.⁴⁶ However, after the CO intermediate is formed, there is little consensus concerning the formation mechanism of C2+ products on an electrocatalytic surface. One potential pathway proposes that C2 products are formed through the dimerization of surface adsorbed CH₂ species whereas another pathway theorizes that C2 products are formed through the dimerization of the CO intermediate.^{47,48} A report by Ma et al. hypothesized that the formation of products containing 3 or more carbons such as npropanol occurred through chain elongation via an adsorbed *HCO species.⁴⁹ This "polymerization" type mechanism is similar to the mechanism accepted for a related process, the Fischer-Tropsch reaction, where syngas (CO and H₂) is thermally reduced to liquid fuels and long-chain hydrocarbons.^{50,51} Catalysts containing cobalt have been reported as active materials for the Fischer-Tropsch and reverse water gas shift reaction which indicates that the adsorption energy of CO₂ and CO on a cobalt surface is favorable.^{52–55} In addition, it was previously mentioned that cobalt sulfides are known to be catalysts for the hydrogen evolution reaction which requires the presence of adsorbed protons. Therefore, it is not unreasonable to hypothesize that the Co₉S₈ catalyst reported here, has the favorable binding energies for both *CO and *H which could promote the formation of C3 and C4 products through a polymerization-like mechanism. However, inoperando studies combined with computational DFT simulations are needed to further elucidate mechanistic insights for the observed activity of the reported Co_9S_8 catalyst.



Figure 3.10: (a) SEM image of a Co_9S_8/Ti electrode post-catalytic testing at -0.49 V vs. RHE. (b-d) SEM-EDS maps of Co, S, and K, respectively for a tested Co_9S_8/Ti electrode. (e) Experimental and simulated XRD pattern for a tested Co_9S_8/Ti electrode. The Ti substrate is indicated by * in the experimental pattern.

After electrochemical testing was completed, the Co₉S₈/Ti foils were characterized to determine whether the nanoparticle film had significantly changed upon applied potential. Figure 3.10a-d shows a representative SEM image and the corresponding SEM-EDS maps. The SEM image shows a roughened surface while the SEM-EDS maps show both Co and S signals evenly distributed across the catalyst film. However, the ratio Co to S changed from nominally 9:8 pre-catalysis to 5:2 post-catalysis. This indicates that sulfur was being removed from the nanoparticle film, possibly as H₂S as is observed with copper

sulfide systems. The XRD of a post-catalysis foil can be seen in Figure 3.10e. The experimental pattern shows the sharp peaks for the underlying Ti foil (denoted by asterisks) and a significant loss in crystallinity for the Co_9S_8 nanoparticles as compared to the precatalysis XRD shown in Figure 3.4e. The post-catalysis XRD corresponds well with the SEM and SEM-EDS data showing that the Co_9S_8 nanoparticles degraded over the course of the 24-hour galvanostatic experiment.

3.4 Conclusions

In this chapter, I highlighted efforts to synthesize and test Co_9S_8 nanoparticles for the electroreduction of CO_2 to make value added products. The Co_9S_8 nanoparticles made through traditional colloidal procedures had a wide variety of particle sizes and morphologies. When tested for CO_2 reduction, the catalysts produced a large range of both gaseous and liquid products, all with low faradaic efficiencies (< 1%). However, these products ranged from C1 to C4 products, with the larger carbon products being particularly interesting. While Co_9S_8 is not an outstanding catalyst for the reduction of CO_2 , the analytes observed, albeit in low quantities, indicate that further modifications and improvements to the catalyst could result in higher achieved faradaic efficiencies. This in turn would open a family of catalysts that potentially do not contain copper that are capable of producing C4 products.

3.5 References

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Chapter 4

Phase-Selective Solution Synthesis of Perovskite-Related Cesium Cadmium Chloride Nanoparticles

4.1 Introduction

All-inorganic metal halide perovskites and perovskite-related phases are attracting significant attention for their intriguing properties such as tunable band gaps¹ and long carrier diffusion lengths.^{2,3} These properties have led to inorganic metal halide perovskites being investigated as promising materials for numerous applications, including solid-state lighting,^{4,5} photocatalysis,^{6,7} photovoltaics,^{8,9} and thermoelectrics.¹⁰ For example, thin films of tetragonal β -CsPbI₃, in combination with a hole transport layer, achieved a high power-conversion efficiency in a perovskite solar cell while also exhibiting high stability under continuous illumination in air.⁹ Additionally, crystals of Cs₂AgInCl₆ doped with sodium and bismuth exhibited white light emission with a high photoluminescence quantum yields and a long lifetime.¹¹ Bulk films and crystals, however, can suffer from low exciton binding energies, and the presence of intrinsic defects can significantly affect the photoluminescence quantum yield.¹² Nanostructured metal halide perovskites can help to circumvent some of these problems.

Over the past few years, the synthesis of nanostructured metal halide perovskites has developed significantly, with diverse synthetic methods producing a broad scope of phases. Solution-based, hot injection methods are particularly powerful, as they permit fine control over nanoparticle size and shape,¹³ including cubes,^{1,14} nanowires,¹⁵ spheres,¹⁶ and platelets.^{13,14} For example, injecting cesium oleate into a hot solution containing octadecene, oleylamine, oleic acid, and an appropriate PbX₂ salt (X = Cl, Br, I) instantaneously forms the desired metal halide perovskite nanoparticles: i.e., CsPbCl₃, CsPbBr₃, and CsPbI₃. The band gaps of metal halide perovskite nanoparticles can be modified, much like for their bulk counterparts, by changing the identity of the halide or using a mixture of halides. This results in highly tunable photoluminescence with narrow emission line widths that span the entire visible spectrum.¹ The ease of synthesis, the ability to fine-tune the band gap and the nanoparticle size and shape, and the high defect tolerance due to the trap states being located in the conduction or valence band^{12,17} make metal halide perovskite nanoparticles of significant interest for a wide range of applications, including light-emitting diodes,^{4,5} photodetectors,^{18,19} and lasers.²⁰⁻²²

Solution-based routes to nanocrystals of all-inorganic metal halide perovskites and perovskite-related phases have been demonstrated to be important and useful. However, these methods are typically limited to a small number of systems that include the A-site cations Rb⁺ and Cs⁺ and the B-site cations Pb²⁺, Sn²⁺, and Ge^{2+,23-26} Additional cations have been incorporated, including Ag⁺, Tl³⁺, Bi³⁺, and In^{3+,27-28} albeit in the doubleperovskite structure. Cadmium-based halide perovskites and perovskite-related phases, which offer unique properties in comparison to their lead halide counterparts, have been studied in the context of doping effects that modify electron paramagnetic resonance and photoluminescent signals, which are important for photon upconversion and higher excited-state luminescence.²⁹⁻³¹ CsCdCl₃ was also considered in the context of a computational screening effort to identify possible metal halide perovskite semiconductors,³² and CsCdBr₃ was studied for its nonlinear optical properties.³³ However, the synthesis of cadmium-based metal halide perovskites and perovskite-related phases has been limited to bulk-scale single crystals,³⁴ rather than solution-synthesized nanoscopic phases.

Here we show that cesium cadmium chloride perovskite-related phases can be accessed through solution-based methods related to those that routinely produce other metal halide perovskite nanocrystals, including CsPbX₃ (X = Cl, Br, I). By dissolution of cadmium chloride in a high-boiling-point organic solvent and injection of a solution of cesium oleate at elevated temperatures, three distinct phases can be selectively synthesized as particles having characteristic dimensions in the range of 75–250 nm. The phase selectivity arises from differences in the local concentration of cesium and cadmium ions, the injection rate of cesium oleate, and the reaction temperature. Hexagonal CsCdCl₃ has a three-dimensionally bonded structure that has two face-sharing octahedra that form $Cd_2Cl_9^{5-}$ subunits, which share corners with six other octahedra (Figure 4.1a); this structure is often referred to as a hexagonal perovskite.³⁵



Figure 4.1: Crystal structures of hexagonal CsCdCl₃ and the Ruddlesden-Popper phases Cs_2CdCl_4 , and $Cs_3Cd_2Cl_7$. The blue, green and red spheres correspond to cesium, cadmium, and chlorine atoms, respectively.

Cs₂CdCl₄ (Figure 4.1b) and Cs₃Cd₂Cl₇ (Figure 4.1c) are Ruddlesden–Popper phases, which are layered intergrowths of perovskite-type cadmium chloride slabs and rock salt type cesium chloride slabs. This synthetic capability bridges the gap between previous syntheses for these phases, which produce bulk-scale crystals using procedures that are not amenable to nanostructuring, and the most commonly used methods for accessing colloidal nanoparticles having tunable morphologies and sizes. All three of these cesium cadmium chloride phases were found experimentally to have band gaps in the range of 4.70–5.13 eV, which places them in a rare category of ultrawide-band-gap materials that are of interest for applications including deep-ultraviolet optoelectronics and high-power electronics.³⁶

4.2 Experimental Section

4.2.1 Materials

Cadmium(II) chloride (CdCl₂, 99.99%) and oleic acid (90%, technical grade) were purchased from Alfa Aesar. Cesium carbonate (Cs₂CO₃, 99+%) was purchased from Strem Chemicals. 1-Octadecene (90%, technical grade) and oleylamine (70%, technical grade) were purchased from Sigma-Aldrich. Solvents (hexanes and ethanol) were of analytical grade. All chemicals were used without further purification. Note that cadmium(II) chloride is a toxic reagent that should be handled carefully using appropriate, established safety protocols that are in accordance with the safety data sheet (SDS).

4.2.2 Preparation of Cesium Oleate

Cesium oleate was prepared using a modified literature procedure.³⁷ In a typical synthesis, Cs₂CO₃ (1.47 g, 4.51 mmol), 1-octadecene (30.9 mL), and oleic acid (14.1 mL) were placed in a three-neck, 100 mL round-bottom flask with a condenser, thermometer adapter, alcohol thermometer, stir bar, and rubber septum. The flask was purged of oxygen by cycling between vacuum and Ar three times. The flask was then heated to 120 °C at 5 °C/min and held at that temperature for 5 h while under a static Ar atmosphere. The solution was cooled to room temperature, and the clear, amber-colored solution was transferred to a septum-capped vial for future use.

4.2.3 Synthesis of CsCdCl₃

CdCl₂ (84 mg, 0.458 mmol) and 1-octadecene (10 mL) were placed in a three-neck, 100 mL round-bottom flask with a condenser, thermometer adapter, alcohol thermometer, magnetic stir bar, and rubber septum. The flask was heated to 100 °C under vacuum for 30 min. After a switch to an Ar atmosphere, a mixture of oleylamine (1 mL) and oleic acid (1 mL) was injected, causing the solution to become clear yellow. The temperature was raised to 300 °C at 5 °C/min, and then 1.4 mL of cesium oleate was injected at a rate of 1.4 mL/min using a syringe pump. Afterward, the reaction flask was placed into a room temperature water bath to cool. The resulting white precipitate was isolated by centrifugation at 13500 rpm for 3 min. The powder was resuspended with a 1/1 mixture of hexanes and ethanol, and the washing procedure was repeated again. The washed powder, which consisted of nanoscopic CsCdCl₃, was stored in hexanes for further characterization.

4.2.4 Synthesis of Cs₂CdCl₄

The procedure was identical with that described above for CsCdCl₃, except that 53 mg (0.289 mmol) of CdCl₂ was used and the temperature was raised to 160 °C at 5 °C/min prior to injecting 1.4 mL of cesium oleate at a rate of 1.4 mL/min using a syringe pump.

4.2.5 Synthesis of Cs₃Cd₂Cl₇

The procedure was identical with that described above for CsCdCl₃, except that 62 mg (0.338 mmol) of CdCl₂ was used and the temperature was raised to 240 °C at 5 °C/min prior to injecting 1.4 mL of cesium oleate at a rate of 1.4 mL/min using a syringe pump. For this reaction, it is important for the solution to change from a clear yellow to a milky white before the cesium oleate is injected. This change should occur around 220 °C.

4.2.6 Characterization

Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance Xray diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) data, including element maps, were collected on a Verios G4 XHR FESEM instrument. Images were collected at an accelerating voltage of 3 keV and a working distance of 2–3 mm, while maps were collected at 10 keV and a working distance of 4 mm. To mitigate charging effects on the Cs₃Cd₂Cl₇ particles, beam deceleration was used to retard the electron beam energy to a landing voltage of 1 keV. For EDS mapping, the L α 1 lines for Cs (4.29 keV) and Cd (3.13 keV) were used while the K α 1 line was used for Cl (2.62 keV). Diffuse reflectance UV– vis spectroscopy data were acquired using a PerkinElmer Lambda 950 UV–vis–NIR spectrophotometer utilizing a 150 mm integrating sphere collecting data from 200 to 800 nm, taking 1 nm steps, and using a 4 nm slit width in the diffuse reflection mode. The reference spectrum for total reflectance (pure white) was measured against a Spectralon disk. A concentrated suspension of nanoparticles was drop-cast onto a glass slide until a uniform, thick, and opaque spot was observed.

4.2.7 DFT Calculations

First-principles calculations were performed to investigate the band gaps and band structures of the hexagonal $CsCdCl_3$ crystal and the Ruddlesden–Popper Cs_2CdCl_4 and $C_{s_3}Cd_2Cl_7$ phases. The self-consistent-field calculations were initially performed at the Perdew–Burke–Ernzerhof (PBE)³⁸ semilocal level of density functional theory using the projected augmented wave (PAW)^{39,40} method implemented in the Vienna Ab initio Simulation Package (VASP).⁴¹ The plane-wave basis energy cutoff was set to 520 eV. Brillouin zones of the perovskites were sampled with Gaussian smearing, with a Γ -centered Monkhorst–Pack grid density of 0.04/Å. The atomic positions and the lattice vectors of the perovskite bulk structures were fully optimized to converge the total energy and force within less than 10–6 eV and 0.01 eV/Å, respectively. For the band structure calculations, on consideration of the known underestimation of the band gap at the semilocal level, the hybrid Heyd-Scuseria-Ernzerhof functional (HSE06)⁴² was applied. The lattice constants that were computationally determined through structure relaxation as well as the simulated lattice constants are shown in Table 4.1. The difference between the calculated and simulated lattice constants was small, ranging from 0.0012 to 0.12 Å. Therefore, both the PBE and HSE06 functionals predicted lattice constants that are consistent with experimental observations.

Table 4.1 : Experimenta	l and computational	lattice parameters
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Material	Exp. a	PBE a (Å)	HSE06 a	Exp. <i>c</i> (Å)	PBE c (Å)	HSE06 <i>c</i>
	(Å)		(Å)			(Å)
CsCdCl ₃	7.58	7.57	7.52	18.87	18.86	18.70
Cs ₂ CdCl ₄	5.26	5.38	5.34	16.88	17.11	17.01
$Cs_3Cd_2Cl_7$	5.24	5.37	5.32	27.24	27.67	27.51

4.3 Results and Discussion

CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇ were synthesized using a solution-based method involving the injection of a cesium oleate solution into a heated CdCl₂ solution, as described in the Experimental Section and outlined in the reaction schemes in Figure 4.2. All three synthesized phases were stable when they were stored under ambient conditions but unstable in highly polar solvents.



Figure 4.2: Reaction schemes for the solution synthesis of CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇.

Figure 4.3 shows the experimental powder XRD pattern for the CsCdCl₃ product, which matches well with the simulated pattern for hexagonal CsCdCl₃.⁴³ The structure of

hexagonal CsCdCl₃, highlighted in Figure 4.1a, shows the two face-sharing octahedra that comprise the Cd₂Cl₉^{5–} subunit mentioned above, which share corners with six other distinct octahedra.⁴⁴ SEM-EDS element maps and spectra, shown in Figure 4.3b and Figure 4.4, confirm that cesium, cadmium, and chlorine were uniformly distributed throughout the sample. There was no microscopic evidence of secondary phases or amorphous components: i.e., no regions have significantly different morphologies or compositions.



Figure 4.3: (a) Experimental and simulated powder XRD patterns for hexagonal CsCdCl₃. (b) Low magnification SEM image and corresponding SEM-EDS element maps for Cd, Cs, and Cl. (c) Higher magnification SEM image showing the spherical morphology of the CsCdCl₃ particles.

The SEM image shown in Figure 4.3c reveals roughly spherical particles with diameters of approximately 100 nm. The isotropic morphology observed by SEM is consistent with

the XRD data, which does not show evidence of a preferred orientation. The particle size observed by SEM is also consistent with the XRD data, which do not have significantly broadened peaks, as would be expected for smaller particle sizes.



Figure 4.4: EDS spectra for CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇ nanoparticles.

When the amounts of cesium oleate and CdCl₂ used in the reaction were changed, as well as the reaction temperature, it was possible to also synthesize two Ruddlesden– Popper phases, $A_{n+1}B_nX_{3n+1}$, in the Cs–Cd–Cl system. Both the n = 1 phase, Cs₂CdCl₄, and the n = 2 phase, Cs₃Cd₂Cl₇, are intergrowth structures of 2D perovskite layers, where n is the number of perovskite layers, interleaved between a rock salt layer (Figure 4.1b,c).⁴⁵



Figure 4.5: (a) Experimental and simulated powder XRD patterns for Cs₂CdCl₄. (b) Low magnification SEM image and corresponding SEM-EDS element maps for Cd, Cs, and Cl. (c) High magnification SEM image showing the micron sized Cs₂CdCl₄ plates and rods.

The experimental XRD and simulated reference patterns of the n = 1 Ruddlesden– Popper phase, Cs₂CdCl₄, are shown in Figure 4.5a.⁴³ The XRD data indicate that Cs₂CdCl₄ formed with no crystalline impurities, and the SEM-EDS element maps and spectra (Figure 4.5b and Figure 4.4) confirm that the expected elements are uniformly distributed. In contrast to CsCdCl3, which produced roughly spherical particles, the Cs₂CdCl₄ particles appear as a mixture of large rectangular plates and rods that have dimensions up to 5 μ m, as shown in the SEM image in Figure 4.5c. The anisotropic morphology observed microscopically, which is expected on the basis of the layered crystal structure, is validated in the bulk sample by the XRD data. In the XRD pattern for Cs₂CdCl₄ in Figure 4.5a, the intensities of the peaks corresponding to the {001} planes are significantly enhanced in comparison to the simulated pattern, indicating a preferred orientation perpendicular to the [001] direction. This preferred orientation is consistent with, and expected for, both platelets and rods which grow such that the {001} planes are parallel to the basal plane. Additionally, the {001} XRD peaks are broadened relative to the other peaks. Scherrer analysis of the {001} peaks indicates an average grain thickness of 11 nm, which is consistent with the anisotropic morphology and provides an estimate for the thickness of the Cs₂CdCl₄ platelets and rods.



Figure 4.6: (a) Experimental and simulated powder XRD patterns for Cs₃Cd₂Cl₇. (b) Low magnification SEM image and corresponding SEM-EDS element maps for Cd, Cs, and Cl. (c) High magnification SEM image showing the Cs₃Cd₂Cl₇ platelets.

XRD data for the n = 2 Ruddlesden–Popper phase, Cs₃Cd₂Cl₇, are shown in Figure 4.6a. A comparison of the experimental and simulated XRD data³⁴ confirms the formation of Cs₃Cd₂Cl₇ with no observable impurities, while the SEM-EDS element maps and spectra in Figure 4.6b and Figure 4.4 indicate that, like the other phases, the three constituent elements are evenly distributed throughout the sample. The SEM image in Figure 4.6c shows that the particles are anisotropic, similar to those of Cs_2CdCl_4 . However, the morphologies of the Cs₃Cd₂Cl₇ particles are noticeably different. The SEM image reveals that most of the particles form rectangular prisms with lateral dimensions ranging from 250 nm to 1 μ m. In contrast to Cs₂CdCl₄, which exhibited a preferred orientation perpendicular to the [001] direction, the {110} family of planes in Cs₃Cd₂Cl₇ have slightly higher relative intensities in comparison to the simulated pattern. While this preferred orientation direction differs from that seen in most layered compounds (i.e., the layer stacking axis), it has been observed in other Ruddlesden–Popper phases as particles and thin films^{46,47} and therefore is not unexpected. In these other Ruddlesden-Popper systems, the observation of a preferred orientation perpendicular to the [110], instead of [001], direction was attributed to the rate of particle growth.⁴⁶ It is possible that the observed differences in morphology and preferred orientation between the Cs_2CdCl_4 platelets and the $Cs_3Cd_2Cl_7$ prisms arises from faster crystal growth kinetics of the $C_{s_2}CdCl_4$ phase, which can be altered through the injection rate of cesium oleate, as discussed in further detail below. It is also possible that slight differences in ligand binding affinities to the exposed facets of Cs_2CdCl_4 vs Cs₃Cd₂Cl₇ could play a role in the observed differences in morphology and preferred orientation.

The phase-selective synthesis of hexagonal CsCdCl₃ and Ruddlesden–Popper Cs₂CdCl₄ and Cs₃Cd₂Cl₇, using the same platform, is significant and important, as different compounds in the same phase diagram typically have different properties. It is therefore useful to identify how subtle differences in reaction parameters lead to phase selectivity. All three reactions involve the same injection volume of cesium oleate, and therefore the cesium reagent concentration remains constant. The key procedural differences, determined on the basis of observations of experiments run under a variety of conditions, involve differences in the concentrations of cesium and cadmium, the injection rate of cesium oleate, and the reaction temperature.



Figure 4.7: Experimental XRD pattern showing a mixture of the cubic and hexagonal CsCdCl₃ phases when slowly injecting cesium oleate at lower temperatures. The simulated reference patterns are also presented on the bottom.

Consider hexagonal CsCdCl₃, which forms as a pure phase when cesium oleate is slowly injected into the solution of CdCl₂ at 300 °C, such that the cesium and cadmium ion concentrations are equivalent. When this reaction is run at a lower temperature, cubic
CsCdCl₃ begins to form, although not as a pure phase; it is always present, in an \sim 1:1 ratio, with hexagonal CsCdCl₃ (Figure 4.7). Hexagonal CsCdCl₃ is the thermodynamically preferred structure, and so its formation at a higher temperature is expected, although the observation of some cubic perovskite-type CsCdCl₃ suggests that this metastable polymorph may be accessible as a pure phase with further optimization. When the injection rate of the cesium oleate into the cadmium chloride is increased significantly, from 1.4 mL/min to 1.4 mL/s, while the same cesium and cadmium ion concentrations and 300 °C



Figure 4.8: Experimental XRD pattern showing a mixture of $Cs_3Cd_2Cl_7$ and Cs_2CdCl_4 after injecting the cesium oleate solution swiftly at 240 °C. The simulated references patterns are also shown on the bottom.

temperature are maintained, Cs_2CdCl_4 begins to form, along with hexagonal CsCdCl_3. Likewise, when the reaction that forms phase-pure $Cs_3Cd_2Cl_7$ is carried out with a faster injection rate (1.4 mL/s instead of 1.4 mL/min), Cs_2CdCl_4 , the most Cs-rich phase, begins to form (Figure 4.8). However, when the reaction that forms phase-pure Cs_2CdCl_4 is carried

out at the faster injection rate, Cs_2CdCl_4 still forms (Figure 4.9). On the basis of these results, we speculate that a faster injection rate increases the local concentration of Cs relative to Cd to begin favoring more Cs rich phases, resulting in the preferential formation of the most Cs rich phase, Cs_2CdCl_4 , at faster rates



Figure 4.9: Experimental and simulated XRD pattern showing nearly phase-pure Cs₂CdCl₄ after injecting swiftly at 160 °C.

of cesium oleate injection. These observations led to the identification of the optimized conditions that were used to generate phase-pure products and also provided some insights into how the various phases form.

CsCdCl₃, which had been previously synthesized as single crystals, was found in several studies to have a band gap that is on the order of 5 eV,^{48,49} which places it in a rare category of ultrawide-band-gap materials. Anticipating that the different Cs–Cd–Cl phases



Figure 4.10: (a) Diffuse reflectance spectra for CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇ particles. (b-d) Tauc plots of CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇, respectively, with the experimental band gap values.



Figure 4.11: Diffuse reflectance spectrum from 200-800 nm for CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇ particles.

would have different band gaps, we used diffuse reflectance UV–vis spectroscopy to determine the optical band gaps of our nanoscopic CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇ materials. The diffuse reflectance spectra for all three phases are shown in Figure 4.10a

and Figure 4.11. The onset of absorption for all three phases occurs in the range of 225–275 nm; Cs₂CdCl₄ has the highest absorption onset at 280 nm, and Cs₃Cd₂Cl₇ has the lowest absorption onset at 255 nm. First-principles calculations were performed to determine if each phase had a direct or an indirect electronic transition. By calculation of the band structures along the high-symmetry directions for all of the crystal structures at the PBE level, hexagonal CsCdCl₃ was found to have a direct band gap, while Cs₂CdCl₄ and Cs₃Cd₂Cl₇ had indirect band gaps (Figures 4.12-4.14). Using the square root



Figure **4.12**: Calculated PBE band structure corrected using a scissor operator with the HSE band gap for CsCdCl₃.



Figure 4.13: Calculated PBE band structure corrected using a scissor operator with the HSE band gap for Cs_2CdCl_4 .



Figure 4.14: Calculated PBE band structure corrected using a scissor operator with the HSE band gap for $Cs_3Cd_2Cl_7$.

or square of the Kubelka–Munk function for indirect vs direct transitions, respectively, the diffuse reflectance spectra were transformed into the Tauc plots shown in Figure 4.10b–d. An analysis of the Tauc plots indicated that the band gaps of CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇ were 5.13, 4.91, and 4.70 eV, respectively. The observed band-gap values for



Figure 4.15: (a,c,e) Computed total density of states of Cl, Cd, and Cs for CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇, respectively. (b,d,f) Computed projected density of states for Cl p, Cs p, Cd s, and Cd d orbitals for CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇, respectively. The insets show magnified projected density of states in order to discern the Cs p, Cd d, and Cd s orbitals.

the cesium cadmium chloride particles are considerably larger than for cesium lead chloride nanoparticles, which have band gaps of around 3 eV.¹ The larger band gaps of the cadmium vs lead compounds are attributed to the larger Cd–Cl vs Pb–Cl electronegativity differences. The experimental band gap for CsCdCl₃, determined here to be 5.13 eV, falls within the previously reported range of band gaps for this material.^{48,49} It is well-known that semilocal (PBE) calculations significantly underestimate band gaps. Therefore, we

employed the hybrid HSE06 functional to achieve higher predictive accuracy. Using this approach, CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇ were calculated to have band gaps of 3.50, 4.20, and 3.43 eV, respectively, and the HSE06 predictions are thus in reasonable accordance with experiments. The experimental and computational band gaps of CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇ are larger than 3.4 eV, which places them in the category of ultrawide-band-gap materials.³⁶ The total and projected densities of states for all three synthesized phases were also calculated (Figure 4.15). It was observed that the valence band edge for the three structures was primarily composed of the Cl p orbitals with some added contribution from the Cd d orbitals. Similarly, for the conduction band edges, the Cd s orbital was the primary contributor, with additional contributions from the Cl p orbitals.

4.4 Conclusions

Three distinct cesium cadmium chloride compounds were synthesized as nanoscopic particles using a low-temperature solution-based method. The hexagonal perovskite-related CsCdCl₃ phase formed as spherical particles and had a direct band gap of 5.13 eV. The Ruddlesden–Popper phases Cs₂CdCl₄ and Cs₃Cd₂Cl₇ formed as anisotropic plates/rods and rectangular prisms and had indirect band gaps of 4.91 and 4.70 eV, respectively. Phase selectivity was achieved through differences in the precursor concentrations of cesium and cadmium ions, the injection rate of cesium oleate, and the reaction temperature. The injection rate, in particular, was found to significantly influence the phase that formed; a faster rate of injecting cesium oleate correlated with the formation of more Cs rich phases, presumably due to higher local concentrations of Cs relative to Cd.

It is anticipated that this phase-selective synthesis could be further developed and modified to produce the types of size- and shape-controlled nanoparticles that are advantageous for applications as light-emitting diodes, photodetectors, and lasers. As ultrawide-band-gap materials, they are especially interesting as potential components for deep ultraviolet optoelectronics, although the toxicity of cadmium may limit their practical utility and/or require methods to ensure stability under operating conditions.

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4.5 References

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Chapter 5

Summary and Outlook

Due to their size-dependent properties, nanoparticles are attractive relative to their bulk counterparts for a variety of applications; however, the scope of materials that can be made through colloidal methods is still rather limited. Therefore, exploring new synthetic methods to expand the library of colloidally accessible materials is crucial. Additionally, to prevent misinterpretation of characterization data for techniques such as XPS and XRD, rigorous procedures concerning data analysis need to be applied. In this dissertation, I have highlighted my efforts towards achieving these goals by: 1) developing methods to synthesize metal sulfide and metal halide perovskite nanoparticles and 2) discussing two different materials characterization techniques, XPS and XRD, and their important role in gaining insights into materials synthesis and design.

Chapter 2 focused on two commonly used characterization techniques, powder Xray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The first part of chapter 2 focused on XRD which is a bulk characterization technique that provides information about the crystalline components within a material. While samples can be straightforward to analyze using XRD, the complexity of experimental patterns can substantially increase when evaluating samples containing nanoparticles. This complexity was attributed to variables such as the nanoparticle's size and shape or the formation of alloys/solid-solutions. Importantly, insights were included on how to best analyze and interpret experimental data using examples from the literature as well as simulated wurtzite CdS patterns. The second part of chapter 2 discussed XPS which is a technique that identifies elements along with their chemical state within the first 3 to 10 nm of a material's surface. The versatility of XPS was demonstrated with three different examples. The first project examined the surface composition of AgRh nanoparticles before and after electrocatalysis. The results showed that the RhO_x species present before catalysis was reduced and the overall metallic ratio between Ag and Rh remained constant which indicated that the material was stable under applied potential. The second project used XPS to investigate the formation mechanism of Pt-Cu₃PdN heterostructured nanoparticles. Aliquots taken at specific points during the reaction allowed for insights into when nitrogen was incorporated into the hybrid particles. In the final example, XPS depth profiling enabled an investigation into the chemical species formed on the surface of Mo₂AlB₂ single crystals after a heat treatment to remove Al. It was determined that a passivating layer of AlO_x approximately 1 to 3 nm thick was preventing further removal of Al from the substrate. This observation proved to be key in determining new synthetic pathways to examine in order to potentially form the desired 2D metal boride, MoB.

XRD and XPS are vital techniques for analyzing and characterizing both bulk and nanomaterials. It should be noted that these two techniques should not be used as a sole characterization technique and instead, are ideally paired with other characterization techniques including electron microscopy (both scanning and transmission) and energy dispersive X-ray spectroscopy to give an accurate representation of the sample. While XRD and XPS are established techniques, there are other aspects that we do not currently utilize that could further assist data analysis. For example, a standard procedure in the solid-state literature regarding when using XRD is to refine an experimental pattern in reference to a calculated pattern and observe its fit. This can be extremely helpful when dealing with convoluted samples and overlapping peaks as can be the case when synthesizing complex bulk materials or colloidal nanoparticles. A drawback for refining experimental patterns, especially for nanomaterials when compared to the bulk, stems from lower signal to noise ratios and reduced accuracy for calculated patterns due to the peak broadening observed at small size scales. In regards to XPS, an interesting area of study could be the investigation of competitive ligand binding on the surface of metals. This information could be useful in designing Janus-like nanoparticles that have two different ligand coatings with differing functionalities. These particles could then be of interest for multi-disciplinary studies including medicinal chemistry and targeted drug delivery as well as site-selective catalysis and click chemistry.

In chapter 3, I discussed efforts to discover new catalysts for the electroreduction of CO₂, specifically looking at cobalt sulfide, Co₉S₈. While copper is the benchmark catalyst for CO₂ reduction due to its ability to produce C2+ products, its high overpotentials and low product selectivity have led researchers to search for materials that improve on these metrics. The presence of chalcogenides on Cu catalysts, either as sulfides or surface adatoms, has been shown to drastically impact the product distribution, shifting it towards formate instead of C2 products such as C₂H₄. Since cobalt has been shown to be a promising transition metal in molecular catalysts for CO₂ reduction, it was hypothesized that cobalt sulfide, Co₉S₈, may be an interesting heterogeneous catalytic material. Phasepure, polydisperse Co₉S₈ nanoparticles ranging from 10 to 110 nm were annealed onto Ti foils. The electrodes were tested in 0.1 M KHCO₃ at a variety of different potentials where the reduced liquid products were monitored by ¹H NMR and the reduced gaseous products were monitored by GC/MS. Though low Faradaic efficiencies were observed (< 1%), the products that were detected included C1 to C4 products. This is an interesting and intriguing result because a heterogeneous cobalt catalyst has yet to be reported for the reduction of CO_2 and few heterogeneous catalysts have been able to produce C3+ products. Therefore, despite the low efficiencies, the observed products hint towards promising future investigations using cobalt based materials for the electroreduction of CO_2 . One direction that could be of potential interest is to make a ternary sulfide that contains both cobalt and an active transition metal for CO_2 reduction. It is well established that adsorbed CO (*CO) is one of the key surface species needed to make C2+ products. Transition metals such as Ag, Au, and Zn selectively produce CO as the binding energies of CO are unfavorable and lead to rapid desorption. Further investigations that look into cobalt chalcogenide materials that include these CO producing metals, in addition to copper, could potentially result in Faradaic efficiency increases for the C2, C3 or C4 products observed for pure Co₉S₈ nanoparticles.

In chapter 4, three distinct phases of cesium cadmium chloride were made as colloidal nanoparticles, hexagonal CsCdCl₃, Cs₂CdCl₄, and Cs₃Cd₂Cl₇. Metal halide perovskites (ABX₃), especially cesium lead halides, have garnered significant attention for their vibrant optoelectronic properties and facile syntheses. While Pb is the primary B-site metal studied in this family of materials, other transition metals halide perovskites, including cesium *cadmium* halides, have been computationally predicted as potentially interesting semiconductors. The synthesized CsCdCl₃ nanoparticles had a direct bandgap of 5.13 eV whereas nanoparticles of the two Ruddlesden-Popper phases, Cs₂CdCl₄, and Cs₃Cd₂Cl₇, indirect bandgaps with magnitudes of 4.91 eV and 4.70 eV, respectively. The phase selectivity observed is hypothesized to arise from differences in the local Cs and Cd

concentrations which were leveraged through variation in the starting precursor amounts, the injection rate of cesium oleate, and the reaction temperature. Most notably, the injection rate seemed to have the largest effect on the formation of phase-pure products where a faster rate resulted in the formation of particles that were Cs-rich due to larger local Cs concentrations. The large bandgaps observed for these materials place the synthesized cesium cadmium chloride nanoparticles in a materials class known as ultra-wide bandgap semiconductors. These materials are hypothesized to have applications in deep UV lasing and light emitting diodes as well as high-power electronics. Though promising, further property characterization of the cesium cadmium chloride family, particularly the thermal and electrical properties of these materials, will need to be explored before their implementation into any application. In the future, it would be interesting to explore possible avenues for post-synthetic modification techniques such as cation exchange on the cesium cadmium chloride structure. The smaller size of the cadmium cation compared to lead, as well as the two different Cd coordination environments within the hexagonal unit cell, could lead to potentially interesting exchange patterns that have yet to observed, thus contributing to the rapidly growing area of nanoparticle cation exchange.

In conclusion, I have discussed my contributions to discover and synthesize a variety of different materials which include but are not limited to sulfides and metal halide perovskites. Furthermore, I briefly highlighted XRD and XPS as two materials characterization techniques that, when used appropriately, are extremely powerful to obtain insights into a materials structure and composition. We hope that the solid foundation of materials, their properties, and characterization techniques discussed in this work will help

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