

Nanostructured Materials for Sustainable Energy: Synthesis, Assembly, and Recovery

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Abstract

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As demand for critical materials rises, sustainable solutions for both recovery and substitution are key to meeting global needs. The electrification of emerging and evolving industries, including transportation and grid storage, will drive a massive increase in demand for high-performance electrochemical materials, as well as create an urgent need for effective recycling methodologies to preserve supply chains. Meeting these challenges requires innovations both in the design of new functional nanomaterials and in the development of efficient, selective recovery systems. To these ends, this thesis presents two complementary projects: the synthesis and characterization of mesophase-forming ultrasmall antimony (III) sulfide (Sb_2S_3) nanoparticles for applications in lithium and sodium-ion batteries and the investigation of crystallization through reaction-diffusion precipitation processes in hydrogel systems for hydrometallurgy separations. Both efforts leverage nanoscale structures and employ small angle X-ray scattering (SAXS) to characterize material structure across length scales. In the first part of this work, a novel, scalable, and room-temperature synthetic pathway to Sb_2S_3 nanoparticles is developed using readily available precursors under open-atmosphere conditions. The resulting nanoparticles spontaneously assemble into stable mesophases exhibiting unexpected rod-like hexagonal packing despite lacking crystallographic registry. SAXS is used to probe the self-assembly of the particles, revealing the influence of ligand chemistry and solvent environment on the assembly process. These ultrasmall particles exhibit high specific capacity, rapid charge/discharge kinetics, and excellent cyclability when integrated into lithium- and sodium-ion battery systems. Next, critical material recovery and

crystallization are explored using hydrogels loaded with selective precipitating agents. Reaction-diffusion coupling within the gels can enable the spatial and temporal encoding of a crystallization pathway. This allows the pathway to be probed using *in situ* ultra-small, small-, and wide-angle X-ray scattering (USAXS/SAXS/WAXS) alongside traditional *ex situ* imaging. The interplay between gel properties, precipitant chemistry, ion concentration, and diffusion behavior is systematically investigated while the crystallization pathway is dissected. This work elucidates how reaction-diffusion dynamics can be harnessed to study crystallization to motivate separation processes. Throughout both studies, SAXS serves as a powerful and versatile characterization tool, enabling high-throughput, *in situ*, and *ex situ* probing of structure and dynamics across scales.

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Stopping by Woods on a Snowy Evening

by Robert Frost, 1923

Whose woods these are I think I know.

His house is in the village though;

He will not see me stopping here

To watch his woods fill up with snow.

My little horse must think it queer

To stop without a farmhouse near

Between the woods and frozen lake

The darkest evening of the year.

He gives his harness bells a shake

To ask if there is some mistake.

The only other sound's the sweep

Of easy wind and downy flake.

The woods are lovely, dark and deep,

But I have promises to keep,

And miles to go before I sleep,

And miles to go before I sleep.

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Chapter 1

Introduction

We can only see a short distance ahead, but we can see plenty there
that needs to be done

—Alan Turing

1.1 The Critical Materials Crisis

One of the most important factors for a nation, or any collection of people for that matter, to consider in securing energy is access to key materials. Despite the increased globalization of markets, and because of it,¹ there is a growing list of raw materials that, when destabilized, can wreak havoc.² As globalization deepens communities' dependence on imported goods, shortages of raw materials in one region increasingly affect supply chains worldwide.³ These disturbances last anywhere from days to weeks or even years. Among the long list of consequences this has, the most prominently felt are inflation and manufacturing disruptions.^{4,5} In the most severe cases, when the affected materials underpin essential infrastructure for power generation, transportation, or telecommunications, this can prevent people from accessing utilities they desperately rely on.⁶

Consider the global semiconductor shortage that began in 2020. Triggered by a convergence of pandemic-driven demand spikes for consumer electronics, factory closures, logistics breakdowns, and rising geopolitical tensions, this single shortage rippled through countless industries.⁷ Automakers were hit hardest, with global vehicle production estimated to have fallen by roughly 15 million units (16%) from 2019 to 2020,

costing the industry several hundred billion dollars in lost revenue.⁸ Factory lines went idle, new car prices spiked, and consumers in dozens of countries faced extended lead times for everything from medical devices to home appliances. The shortage was a stark demonstration of how a deficit in components dependent on a small handful of critical materials can paralyze entire sectors of the global economy. It also drew attention to a larger vulnerability beneath the devices: the critical materials on which this technology relies.

The United States of America publishes a list of critical materials that are important for a wide variety of sectors, with energy represented most prominently.⁹ A material earns the “critical” label when it satisfies, broadly, three conditions: it is difficult to substitute, difficult to acquire, and necessary for a key application. The first condition is technical. Critical materials tend to occupy roles in highly engineered systems where their physical, chemical, or electronic properties are not interchangeable with those of more abundant elements. The second condition is geographic and economic. Most critical materials are mined or refined in only a few countries, often by an even smaller number of companies, leaving the global supply chain dependent on the political and economic stability of just a few entities.¹⁰ The third condition follows from the first two: when supply is concentrated and substitutes are unavailable, even a modest disruption, such as a strike, an export ban, a natural disaster, or a war, can remove a material from the global market on a timescale far shorter than the years required to bring new mines or refineries online.¹¹ As of the most recent assessment, the list of critical materials includes 50 mineral commodities, ranging from familiar elements like lithium, cobalt, and nickel to lesser-known but equally vital materials like gallium, germanium, and the rare earth elements.⁹ Their applications span semiconductors, permanent magnets, batteries, photovoltaics, and defense systems. Essentially, every technology that defines a modern, low-carbon economy.

The concentration of critical materials into a few geographic locations also exposes supply chains to the risk of collapse. Cobalt is perhaps the most extreme example. Coinciding with the rising demand for lithium-ion batteries, demand for cobalt has tripled over the last decade and is set to double again by 2035.¹² Most countries are forced to import their cobalt as more than half (54%) of the global cobalt supply is mined and exported from the Democratic Republic of Congo (DRC) by a handful of international companies. This is then followed by refinement in China (46% of global supply).¹³ This concentration of resources to just a few geographic locations and companies means that the supply chain is at a much greater risk of destabilization than other raw materials with more diversified supply chains. The DRC is also at greater

risk of destabilization than other regions due to a history of geopolitical conflict and economic collapse.¹⁴ It should also be noted that cobalt is rarely mined in concentrated ores. Most production occurs as a by-product of copper and nickel mining.¹³ Meaning that disruptions to the copper and nickel supply chains, even by way of downstream supply and demand fluctuations, are intrinsically linked to cobalt. This makes for a complicated web of interdependencies. It is also impossible to overlook the added moral consequence of mining in the DRC. Approximately 20% of the production is outsourced to artisanal workers, which, combined with lax labor restrictions, means child labor is rampant. In the DRC alone, there are an estimated 40,000 children mining cobalt with little to no safeguards in place.¹³ This situation will only worsen as demand increases.

This story is mirrored for many other critical materials such as graphite,¹⁵ gallium,¹⁶ and rare earth elements;¹⁷ these specific elements being especially critical for transition to renewable energies.¹⁸ Graphite specifically faces challenges as almost every lithium-ion battery uses 100 mesh sized graphite as the anode.¹⁹ This graphite accounts for 10-30% of a battery's weight depending on its construction.²⁰ As such, it is relied upon by much of the world for electrochemical applications, but is important or critical for many applications as well.^{15,18,20,21} Graphite is formed naturally when high temperatures in sedimentary rocks turn plant matter into loosely stacked honey combs, but it can also be synthesized. Naturally formed graphite is cheaper than synthetic, but their distinct attributes are important for their different electrochemical storage technologies, meaning both are required materials.²¹ Over the previous decades, most of the world has scaled back graphite production with the exception of China. Currently, China's production of graphite is 59% of global production, with the next four largest producers barely exceeding a quarter of global production combined.²² This poses a great deal of risk for global supply for the same reasons that a concentration of production and refinement is debilitating for the supply of cobalt.

The transition to renewable energy sources like wind and solar has only intensified this problem. Compared to fossil fuel infrastructure, low-carbon technologies are significantly more material-intensive: a single onshore wind turbine requires roughly nine times more mineral input than a comparably sized gas-fired plant, and an electric vehicle requires six times the mineral content of a conventional internal combustion vehicle.²³ The materials in question are also disproportionately drawn from the critical list. In other words, while decarbonization is of absolute importance to combat climate change,²⁴ it will not solve the inherent

reality that we live on a planet of finite resources. We must pursue holistic solutions.

Faced with these vulnerabilities, what can be done? At the level of national policy, the main strategy for alleviating supply risk is diversification in the geographic sourcing of raw materials and in the firms that process them. However, it is not always feasible to expect that new sources of raw materials can be pulled out of thin air, whether that be a new chemical plant or the opening of a mine. Bringing a new mine online can take a decade or more between exploration, permitting, and construction, and refining capacity faces similar timelines. This varies per region, but establishing a mine was found to take, on average, 13 years in the United States, 17 years in Australia, and 18 years in Canada.²⁵ Geographic diversification, then, is a long-term strategy that does little to address near-term supply shocks. It also does not address the simple fact that critical materials are not uniformly distributed, and not every region can mine its own materials. This is why the creation of circular economies, defined by the recycling of critical materials, is important to develop. The promise of a circular economy is twofold: it reduces the need for primary extraction with all of its geopolitical and ethical baggage, and it gradually decouples a country's material security from the geological accident of where ores happen to be deposited. Lithium-ion batteries (LIBs) exemplify a case where a circular economy is desperately needed. Currently, 95% of LIBs are not recycled.²⁶ Recycling capacity is one large part of this. LIB production is expected to exceed 1 million tons while recycling capacity is estimated to be only 400,000 tons with the majority of this in East Asia and Europe; 219,000 and 110,000 tons respectively.²⁷ This problem of recycling capacity is predominantly a fundamental one; the technologies do not exist to extract most battery materials in a way that is profitable and energy efficient.²⁸ Energy efficiency is a critical requirement of battery recycling as the goal of a circular battery economy cannot be achieved if extracting the relevant materials uses more energy than it is worth. This is why fundamental research into energy-efficient strategies for material extraction is so important, along with the replacement of difficult-to-separate materials with those that are easily extracted where relevant. The problem then is as much one of a lack of technology as it is of poor policy.

1.2 Mitigating Criticality

The task of solving the critical materials crisis lies with the material, chemical, and engineering sciences. The technical work of mitigating critical material risk ultimately reduces to three intertwined research

thrusters: substitution, recycling, and efficiency. Substitution asks whether a critical element can be replaced, either elementally or through a redesign of the host material, without sacrificing the performance that made it critical in the first place. Recycling asks whether materials in end-of-life products can be recovered with energy and chemistry costs low enough to compete with primary extraction. Efficiency asks whether the same function can be delivered using less of the critical element to begin with or by improving the lifetime of the device, which reduces demand. None of these are easy solutions, and none can be solved by policy alone. They require sustained investment in the kind of fundamental science that turns a constrained, geopolitically fragile resource into one that a society can use, reuse, and ultimately depend on.

1.2.1 Substitution

While other materials commonly experience shortages like petroleum,²⁹ food, or water,³⁰ these are often still defined as 'non-critical' on a global scale. Critical materials, by contrast, are inherently more prone to destabilization and often have fundamental properties that make them difficult to replace. Especially in highly engineered applications like tech and clean energy, which rely on highly specialized tooling and expertise to manufacture devices. In these sectors, the manufacturing pipeline is like a Jenga tower, with the material seated squarely at the base. Replacing this foundation might require an entire redesign of the tower that sits on top of it. An example is cobalt substitution in lithium-ion battery cathodes. Commonly used battery chemistries at the cathode are oxides called NMC ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$) and NCA (LiNiCoAlO_2). Cobalt is widely targeted for replacement because of how costly it is, how difficult it is to obtain, and how ethically fraught mining it is. However, replacing cobalt is incredibly challenging, as it is a critical component that structurally stabilizes the cathode as it cycles.³¹ Changing the bulk properties of the material can also change the way that it is handled in the manufacturing process. A slurry made from a different battery chemistry might behave differently while it is being deposited, making it necessary to re-optimize the coating process. This sends a shock wave down the entire assembly line. Substituting the cobalt with another element also results in wildly different battery performance,³² which makes for cycling instability and safety risks. This is why there are always significant hurdles to overcome when substituting a critical material.

This is ultimately why new fundamental material technologies are so few and far between. It can take

anywhere from 5 to 15 years to take a material from 'molecule to market',³³ a timeline that is exorbitantly costly for industries to take on. Replacing critical materials with more economically stable options has not yet become financially sound behavior either, given the poorer performance of current alternatives and the relatively low cost of many critical materials themselves.^{34,35} The burden of innovation therefore falls not on industry but on academia. Encouragingly, the rise of accelerated materials discovery suggests there will be no shortage of prospective alternate materials entering the pipeline.³⁶ The bottleneck, however, has shifted: most promising materials fail to reach industry not because of their properties or performance, but because of their translation; either the material proves difficult to manufacture at scale,^{37,38} or the value it offers does not offset the risk of investment.^{39,40} The result is a 'Valley of Death' in which academic research funding dries up before the technology achieves a foothold in the market.⁴¹ Closing this gap requires fostering an environment in academia that actively develops and supports researchers interested in taking their work to market,⁴² beyond merely funding the underlying science. Programs of this kind are becoming more common at the university and national lab level and have so far been widely successful.⁴³ In the United States, at the federal level, a successful example is NSF I-Corps, which since 2012 has trained over 2,500 teams and produced nearly 1,400 startups that have collectively raised more than \$7 billion in follow-on funding for student ventures.⁴⁴

1.2.2 Recycling

The most important waste stream to recycling technologies regarding critical materials is electronic waste, or e-waste.⁴⁵ E-waste is a large umbrella term that encompasses personal computers, mobile devices, batteries, televisions, and appliances, among others. The scale of global e-waste generation is enormous, with 62 million tonnes being generated in 2022, equaling an estimated \$91 billion USD worth of metal alone.⁴⁶ In 2022, the mass of e-waste per year was up 82% since 2010 and is increasing approximately 5 times faster than the rate of e-waste recycling. Out of this, end-of-life electric vehicles and their storage batteries are projected to become the largest source of e-waste by 2035 and by 2050 will represent 90% of all e-waste feedstocks.⁴⁷ It is also important to know that given the rise of new battery chemistries like lithium iron phosphate (LFP), which are lower in material value than currently common electrodes like lithium-nickel-manganese-cobalt (NMC), it is not guaranteed that current recycling technologies will be economically

viable in the future.^{47,48} Globally, Asia generates the most e-waste by tonnage (30 Mt, 48.4% of global), followed by the Americas (14.1 Mt) and Europe (13.1 Mt).⁴⁶ Recycling, however, diverges sharply from generation. Europe leads on every metric: it generates the most e-waste per capita (17.6 kg) and also recycles the highest share, with a documented collection and recycling rate of 42.8%, roughly 5.6 Mt per year.⁴⁶ The Americas follow at around 30%, while Asia formally recycles only about 12% of its e-waste despite producing nearly half the global total, and African countries recycle less than 1%.⁴⁶ China is the world's single largest e-waste generator at 12 Mt in 2022,⁴⁹ though it also boasts the largest battery recycling capacity of any nation.⁴⁷ The countries with the highest formal recycling rates share a common regulatory toolkit: producer-pays financing (extended producer responsibility), mandatory collection targets, treatment standards for waste streams, co-location of recycling with manufacturing, and adherence to prohibitions on hazardous-waste export to lower-income regions.^{50–52}

In theory, valuable elements are infinitely recyclable. However, issues arise in making perfect recycling a reality that stem from social behavior, product design, recycling technology, and thermodynamics.⁵³ Some materials and the products they are used in lend themselves to ease of recycling. These are usually the most profitable recycling industries which include many of the bulk metals like iron, copper, aluminum, lead, nickel, and zinc which have global recycling rates near or above 50% of the total consumption.⁵⁴ Specialty elements, however, like the rare earth elements (REEs), have global average recycle rates near zero. Figure 1.1 shows the average global recycle rates as of 2022 for 69 of the elements in the periodic table. Elements in gray have insufficient data.

The most significant trend in the recycling of elements is the lack of global recycling of the lanthanide series despite their criticality for a variety of technologies and industries.⁵⁵ NdFeB magnets, for instance, are the strongest magnets commercially available and are key components for direct-drive generators in wind turbines, and synchronous traction motors in battery and hybrid electric vehicles.^{56,57} The most significant reasons why REEs are so poorly recycled are inefficient collection, technological difficulties, and a lack of financial incentive.^{58,59} As is usually the case, the lack of financial incentive and the technological challenges with recycling REEs go hand in hand. Improvements in REE recycling technology will undoubtedly be necessary to lower the associated costs and unlock commercially successful ventures. Ultimately, improving separation and recycling technologies across the board will lower regional dependencies on specific critical

Ultimately, economics will be the driving force for the continued implementation of recycling centers, and improved technologies that reduce costs will drive the economics. It is essential then that just like with substitution, fundamental research and translational development should be implemented for critical material recovery technologies as they have a proven impact.^{48,53,58,63} In addition, researchers should give attention and recognize the added value of using materials that aren't just sustainable and nontoxic, but are actually easy to recycle and separate. While high entropy materials are interesting, and composition is a great way to tune properties, we should place additional value on materials that are easy to integrate into a truly circular material economy.

1.2.3 Efficiency

Within the wider realm of ways that we can address the problem of critical materials there is the nebulous concept of improving efficiency. It should not be surprising that the ways in which we utilize our critical resources are, by and large, inefficient. This is a significant problem, but also an economic and sustainability opportunity. There are many ways that this can be addressed, with the most obvious solution being simply reducing the amount of a given critical material that we use for an application, thus reducing our reliance on these materials. What this looks like depends on the industry, but electrochemical energy storage provides a straightforward example. In lithium-ion batteries, the most expensive component by raw material cost is the cathode. A common cathode chemistry is NMC which contains nickel, manganese, cobalt, and lithium. Over roughly fifteen years, NMC cathodes have been progressively re-engineered to store more energy with less material. The first commercial formulation, NMC111, used nickel, manganese, and cobalt in equal ratios, hence the 1:1:1 naming convention. Successive generations (NMC532, NMC622, NMC811) have driven the cobalt fraction down from roughly one-third of the transition-metal content to about one-tenth, while simultaneously raising the specific capacity (the amount of energy stored per unit mass) from approximately 160 mAh g⁻¹ to 200-220 mAh g⁻¹.^{64,65} The increase in capacity alone is a worthwhile pursuit since it effectively shrinks the battery mass needed for an application,⁶⁶ but the reduction in cobalt has also been beneficial. Cobalt is the most costly and supply constrained material in battery architecture, so reducing dependence on it directly addresses its criticality.⁶⁴ These improvements in electrode chemistry, which also coincided with more efficient manufacturing, helped drive average lithium-ion pack prices from over \$1,100

USD per kilowatt-hour in 2010 to approximately \$110 USD per kilowatt-hour in 2025, a ten-fold reduction, while energy density also continued to rise.⁶⁷

Sometimes, improvements to a device's critical material footprint come with improvements in the device's lifetime as well. Overall, longer lasting devices are a benefit because they reduce the overall demand for critical materials by lowering the need for replacements.⁶⁸ In a perfect world, industry and sustainability efforts would be aligned in this goal of improving lifetimes, but strategies involving the planned obsolescence of a device are often more profitable as they require customers to continue replacing or upgrading their devices. Light bulbs are the most famous example where producers colluded to reduce the life of the light bulbs they sold, with penalties for producers that sold light bulbs that lasted too long, in an effort to improve profits.⁶⁹ Though the efficiency trade-offs of filament design mean the case is debated, internal correspondence and a later US court ruling point to a profit motive.⁷⁰ Despite these pressures from industry, it is important to continue to improve device lifetimes to ease the demand of critical materials. With respect to electric vehicles, some studies actually predict an overall decrease in the entire global demand of cobalt (22% decrease by 2040) should electric vehicle battery lifetimes continue to increase and low-cobalt chemistries be favored.⁷¹ This would require that the average electric vehicle battery lifetime reach 18.1 years by 2040 whereas estimates of lifetimes today are approximately 10 years.^{72–74} This illustrates both the massive scale at which electric vehicles affect the critical materials economy, as well as how impactful longer device lifetimes can be. Alternatively, there are many cases where the component containing the expensive and critical materials can be repurposed for a different device, which also counts towards extended lifetimes. For instance, as renewable energy sources like wind and solar become more widespread, stationary electrochemical energy storage will become increasingly necessary and in demand to make the most of the fluctuating energy production. It is estimated, though, that reusing electric vehicle batteries that are 60-80% of their initial capacity for stationary storage can exceed even the most ambitious predictions for stationary storage demand.⁷⁵ One study showed that if 40% of end-of-life electric vehicle batteries in the European Union were to be repurposed in this way they would match storage demands by 2040, and exceed them two-fold by 2050.⁷⁶

Electrochemical energy storage has been a useful example of the impact of improving device lifetimes, but the same strategies are not transferable to all other sectors. Magnets that make use of rare earth elements

(e.g. Nd, Dy, Sm, Tb) are one such instance. To improve the time in circulation of these elements, the limiting factor is not their chemical stability like it would be in a battery. Rare earth magnets keep their properties for many decades,⁷⁷ and it is because of this that the device, which is usually a motor or turbine, fails long before the magnets inside degrade.⁷⁸ Because of this, the greatest need for improvements in the efficiency of magnet circularity is not at the material performance level, it is at the device and eventual recycling stages of their lives. And the clock is ticking, as demand for electric vehicles and turbines continues to climb, demand for critical materials climbs as well. Most electric vehicles on the road today and tomorrow have an estimated 9-13 year lifespan. Which means in the 2030s we will begin seeing the first large influx of motors and batteries containing critical materials enter waste streams, while most wind turbines and power generators will begin to reach end-of-life by 2040.⁷⁷

1.3 Summary and Outlook

The transition to greener energy sources brings with it the burden of finding sustainable and long-lasting replacements for the materials we use and the opportunity to extract and recycle critical materials that would otherwise exit our not-so-circular economy. There is an incredible opportunity for a material scientist to contribute to the betterment of our planet's resource economy by addressing the three nebulous and interconnected topics of substitution, recycling, and efficiency within critical materials and their devices. The work communicated in this thesis is motivated by addressing these overarching aims. In chapter 4, I present our work in developing a novel synthesis of ultrasmall antimony(III) sulfide nanoparticles that show impressive cycling rate capabilities and a ligand-dependent performance as a lithium and sodium ion anode material.⁷⁹ This material could function as a replacement for graphite in high-power applications that would otherwise rapidly degrade the anode under extreme currents. The synthesis is also highly amenable to scaling, and we utilize small-angle X-ray scattering to interrogate the ligand-dependent particle assembly in solution. In chapter 5, I present our work utilizing hydrogels to study the possible separation of critical materials from a mixed feedstock using reaction-diffusion precipitation chemistry. This work demonstrates the utility of reaction-diffusion coupling as an investigative technique that spatially encodes the stages of crystallization, displaying the history dependence of crystallization. Additionally, in chapter 6 I present ongoing work extending the reaction-diffusion coupling method of investigating crystallization into a system

using mixed feedstock of both nickel and cobalt to identify exploitable phenomena in their separation.

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Chapter 2

Theory

2.1 Precipitation

God made the bulk; surfaces were invented by the devil.

–Wolfgang Pauli (attributed)

2.1.1 Nucleation

Nucleation is the process by which a more stable secondary phase forms its first fragments, nuclei, inside a parent phase. This process can appear in various contexts, including the freezing or melting of a liquid,¹ the transition between two crystal phases in a solid,² and chemical reactions where the product is unstable in the phase of the reagents.³ This chapter will discuss nucleation and growth of an intruding phase predominantly through this chemical reaction lens. These systems are typically well described by monomeric addition. This is where individual building blocks (monomers) such as ions or molecules that are dissolved into the parent phase attach to one another to form the secondary. Nucleation in this way can be broken down into two main types: primary and heterogeneous nucleation. Homogeneous nucleation, or primary nucleation, consists of nuclei, or seeds, forming within the bulk of the parent phase. Heterogeneous nucleation occurs when there is a surface, impurity, or grain boundary not part of the parent phase that facilitates nucleation. Heterogeneous nucleation is almost always more thermodynamically favorable than primary nucleation, as nuclei have a lower surface area while in contact with a foreign body.

Heterogeneous nucleation is therefore defined by the presence of a foreign body, which lowers the energy needed for monomers to nucleate. There are numerous ways this foreign body could manifest, but most can be defined as simply a surface, or rather, a defect on an otherwise featureless surface. This can be seen when a carbonated drink is poured into a scratched glass. The carbon dioxide bubbles form only on the defects in the otherwise smooth glass. Experimentally, it is possible to mitigate these heterogeneous nucleation events, such as by using pristine glassware and pure liquids, but impossible to eliminate.⁴ As such, a correction factor is typically applied to the nucleation rates derived from a classical thermodynamic description.⁵

Primary nucleation can be described thermodynamically by considering the total Gibbs free energy of a nascent particle.³ The total free energy, ΔG_T , is the sum of the surface free energy, ΔG_S , and the volume or bulk free energy, ΔG_ν . The bulk free energy is the difference between the free energy of a system containing a nucleus of n monomers and that of the homogeneous parent phase. The surface free energy is the excess free energy per unit area required to establish an interface between the nucleus and the parent phase. In this description, monomers from the parent phase attach to one another to form a spherical nucleus with a certain radius. A positive ΔG indicates that it is less thermodynamically favorable, while a negative ΔG indicates that it is more favorable. The bulk is always negative, and the surface is always positive, while in a regime where it is possible for phase separation to occur.⁶ This can be seen in the equation for the expression of the free energy of a crystal, $\Delta\mu$ (Eq. 2.1), also known as the chemical potential, where k_B is the Boltzmann constant, T is temperature, and S is the saturation defined by C/C_{sat} which is the monomer concentration divided by the equilibrium monomer concentration of the bulk solid. The surface free energy, ΔG_S (Eq. 2.2), is calculated simply with the surface area of a spherical particle with radius r and surface energy γ . This makes the total energy of a spherical nucleus the sum of both terms (Eq. 2.3) where ν is the molar volume of the monomer in the bulk which converts the chemical potential into energy density.

$$\Delta\mu = -k_B T \ln(S) \quad (2.1)$$

$$\Delta G_S = 4\pi r^2 \gamma \quad (2.2)$$

$$\Delta G_T = 4\pi r^2 \gamma + \frac{4\pi r^3}{3\nu} \Delta\mu \quad (2.3)$$

One should notice from these equations that the bulk free energy is, in fact, always negative and grows regarding the particle radius cubed. The surface free energy, meanwhile, is always positive and grows with respect to the radius squared. Because of this, the total free energy curve must have a global maximum. Equations 2.1-2.3 are plotted in Figure 2.1 demonstrating this for the case study of gold nucleation. A gold atom has a volume, ν , of 0.017 nm^3 and a surface free energy, γ , of 1.5 J/m^2 .^{7,8} The change in surface free energy and bulk energy for a gold nucleation (Figure 2.1A) are calculated at room temp ($T = 298 \text{ K}$) and with a saturation of 1×10^4 which is on the lower end for a solution phase precipitation reaction but gives a reasonable critical radius of 1.35 nm regardless.⁹ The maximum in ΔG_T occurs at the critical radius, r_{crit} , the only stationary point of the curve. Below r_{crit} , the surface term dominates and ΔG_T increases with size, so a nucleus lowers its free energy by shrinking and ultimately redissolving into the parent phase; above r_{crit} , the bulk term dominates and ΔG_T decreases with size, so the same nucleus lowers its free energy by growing. A nucleus at exactly r_{crit} sits at unstable equilibrium, and any fluctuation in size commits it to one path or the other. The barrier height, ΔG_{crit} , is therefore the activation energy that a subcritical cluster must overcome through thermal fluctuations to nucleate.

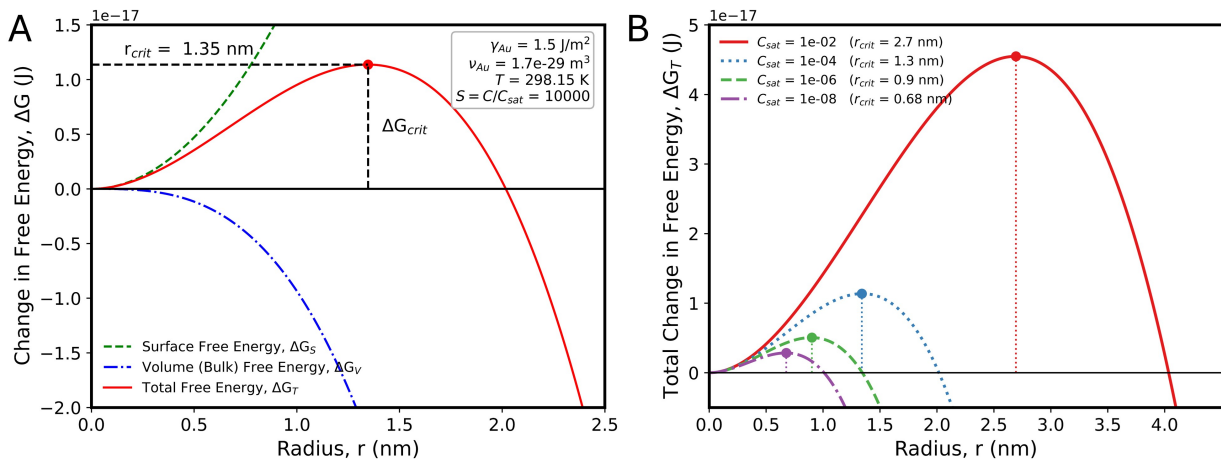


Figure 2.1: **A)** Using the properties of solid gold with an atomic volume of $\nu = 0.017 \text{ nm}^3$ and surface energy of $\gamma = 1.5 \text{ J/m}^2$, the bulk, surface, and total energy is calculated using classical nucleation theory at room temperature given an arbitrary saturation coefficient ($S = C/C_{sat}$). The total energy is plotted with respect to the radius of a nuclei of pure gold. Classical nucleation theory becomes less accurate when the size of the atoms is appreciable to the size of the nuclei, which this system is close to. The critical radius, r_{crit} , and the critical energy, ΔG_{crit} , are marked. **B)** The total free energy with respect to particle radius is plotted for various values of S by changing the saturation concentration, C_{sat} , at a fixed concentration, C .

This classical description stipulates that there are three ways in which the primary nucleation of particles can be controlled experimentally. First is by temperature, second is by saturation, and third is by surface energy. In the case of a simple precipitation reaction, temperature and saturation should be intuitive in that heat and additional monomers can simply be added to the solution. There is subtlety in controlling the surface energy, however. This could be done several different ways such as using organic ligands, ions, or even other surfaces to passivate the nuclei's surface, reducing the critical radius of nucleation, and thereby increasing the rate of nucleation. The effect of the saturation on the critical radius of a nuclei is demonstrated in Figure 2.1B where a range of C_{sat} values are used to calculate the change in free energy with respect to nuclei radius. During a typical reaction that precipitates gold, the reduced Au^0 monomers are incredibly insoluble in water, making it possible to precipitate with incredibly small nuclei. For syntheses that solvate the monomers using ligands, the solubility can be much higher, which increases the critical radius and dramatically increases the energetic barrier. This classical model begins to break down, however, when the atomic radius becomes appreciable compared to the critical radius, but it can still be used for comparative assessments.

Saturation is the foundation of the LaMer model for nucleation and growth by monomer addition during a chemical reaction,¹⁰ which has since been applied quantitatively under specific conditions and proven qualitatively useful in describing many other nucleation events.¹¹ LaMer proposed that there were three fundamental regimes during the nucleation of a phase following the addition of monomers to a solution. Plotting the reaction time against the concentration of monomers in solution makes these regions evident (Figure 2.2). In the first region (I), monomers are added, and they quickly join the parent phase until they pass the saturation concentration, C_S , and reach the minimum concentration for nuclei to form, C_{min} . After this concentration is reached (II), homogeneous nucleation occurs rapidly in a 'burst.' LaMer assumed that this region was nearly instantaneous, and, as such, his model does not account for its kinetics. There is a brief period in this region where the concentration of monomers is high enough to generate nucleation, after which monomers are consumed and nuclei can no longer form. Instead, monomers attach to nuclei in a state of diffusion-limited growth (III). The rate of growth of the nuclei is determined entirely by the transport of monomers to the surface during this time, until the concentration of monomers reaches the saturation point (C_S).

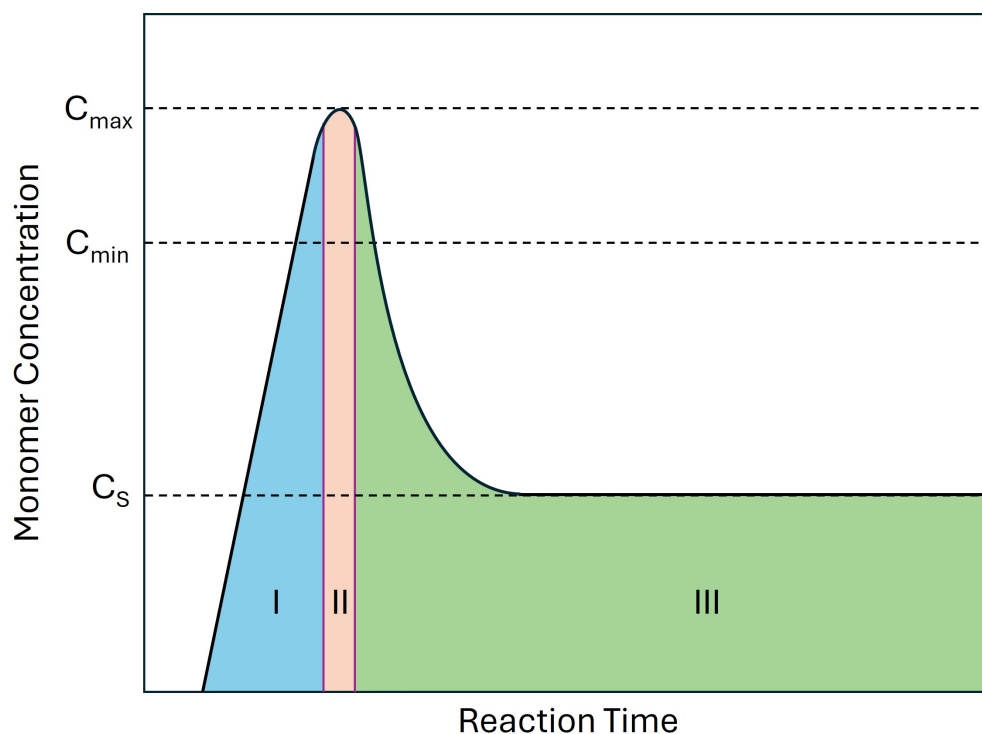


Figure 2.2: A plot of the LaMer model for burst nucleation of a phase for explaining nucleation and growth from a solution of monomers.¹⁰ The LaMer model is broken into three regions: I) monomer generation, II) nucleation, and III) growth and ripening.

LaMer's model assumes a reversible process where monomers that joined the nuclei can dissolve again. This is governed by the solubility of the monomer in the parent solution (Eq. 2.4) and is why in Figure 2.2 the curve levels out so that monomer concentration in solution becomes constant with respect to reaction time. It is common for the solubility of the monomer to be so exceedingly small that there are effectively no monomers left in solution after growth has concluded.

$$nM \rightleftharpoons M_n \quad (2.4)$$

2.1.2 Growth

Classical Growth

After nucleation, a particle is established, and the attachment of solvated monomers is akin to heterogeneous nucleation. However, the classical description of particle nucleation and growth (Figure 2.1) predicts that

larger particles will necessarily be more stable than smaller particles due to the bulk being lower in energy than the surface. This results in the phenomenon of the smallest particles, those with the highest curvature, preferentially re-dissolving into solution, while the largest particles, those with low surface-to-volume ratios, are more stable. This allows the largest particles to continue to grow. This coarsening of sizes is referred to as Ostwald ripening, as the phenomenon was first described by Wilhelm Ostwald in 1900,¹² and later mathematically refined by Herbert Freundlich in 1909.¹³ The resulting Ostwald-Freundlich equation describes the boundaries between phases and relates the chemical potential to curvature. Where in Equation 2.5, $C(R)$ is the equilibrium solubility of a particle of radius R , and C_∞ is the equilibrium solubility (or chemical activities) of the species (as a flat surface, when the radius is infinite), V_{atom} is the atomic volume, γ is the surface tension, k_B is the Boltzmann constant, and T is absolute temperature. The equation describes how much more soluble a curved particle is relative to a flat surface of the same material. The result is an equation relating the equilibrium solubility of a particle of radius R to that of a flat interface of the same material. Because R appears in the denominator of the exponent, the enhancement is largest for the smallest, most highly curved particles and decays toward unity as R grows, so smaller particles are always more soluble than larger ones of the same composition.

$$\frac{C(R)}{C_\infty} = \exp\left(\frac{R_{\text{critical}}}{R}\right) \quad (2.5)$$

Where R_{critical} is defined as

$$R_{\text{critical}} = \frac{2\gamma V_{\text{atom}}}{k_B T} \quad (2.6)$$

The eventual result of Ostwald ripening is that solutions with small enough particles will tend towards a broader size distribution initially but ultimately coarsen into fewer, larger particles. This is a slow process at room temperature for solid particles, on the order of weeks or months in solution, but it becomes more pronounced both at higher temperatures and smaller sizes. Though there are examples of Ostwald ripening being leveraged, or perhaps combated, with careful control of sacrificial particles,¹⁴ or monomer concentration.¹⁵ This size focusing happens when the monomer concentration is high enough that the particles are under diffusion-limited growth. Since the largest particles will exhaust the monomers nearest to them, the smaller particles tend towards faster growth. In colloidal nanocrystal systems, this is especially pronounced

as surface ligands slow the diffusion towards the surface from the bulk fluid.

Regardless of diffusion or reaction-limited growth, once a monomer makes it to the surface of a solid precipitate, its attachment to the surface is dependent on the crystallography of the particle, or rather, the arrangement of atoms already present. This is the predominant method of shape development in crystal growth. An incoming monomer can attach to any empty site on the surface of the solid, which means that crystal facets with more empty sites will grow more quickly than facets with fewer. These empty sites are where the attractive forces are greatest, and occur predominantly at steps, dislocations, and edges where multiple monomers surround the site.⁶ Monomers can also land temporarily onto a surface before they eventually find a thermodynamic minimum in an active site. Figure 2.3 shows these active sites where a monomer might minimize the exposed surface and passivate the nearest neighboring blocks. This is Kossel's 1934 model,¹⁶ and hinges on the idea that the crystal surface is not in fact pristine, but is made up of steps, edges, and surface vacancies. These sites are preferable to a monomer compared to a pristine surface.

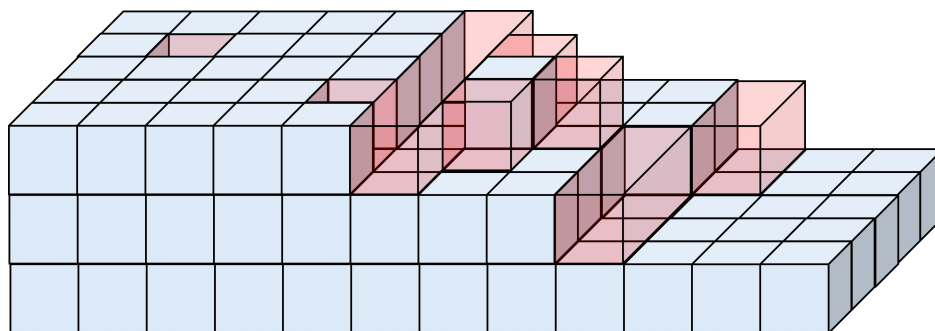


Figure 2.3: Simple model of an imperfect crystal covered in steps, edges, and surface vacancies. The red areas are active sites where an incoming building block would be able to rest in a local thermodynamic minimum

In the case where the facets of a crystal are effectively uniform in the number of active sites, no facet will grow faster than any other and the shape of the crystal will tend to be more isotropic, or even spherical. This is a simplification, and more in depth handling can be found in Mullin (2004).⁶ The morphology, or habit, of a crystal is determined by a difference in growth rates along crystallographic directions. According to Bravais, the crystal facets with the highest reticular densities (the largest number of sites) and smallest interplanar distances, d_{hkl} , grow the slowest and direct the morphology.¹⁷ While this rule is too simplistic to predict every crystal habit, it forms a firm basis. The most accurate models take into consideration the bonding energies of the crystals, the interactions of solvent and additive molecules at the crystal surface,

and the diffusion and kinetics of growth unit attachment.¹⁸

With this in mind, there are a number of strategies that are employed to control the shape of crystals. The most typical is controlling the concentration of precursors over time. After nucleation, the production and consumption rates have a strong influence on growth, as the fast addition of monomers tends to produce more anisotropic shapes.¹⁹ Slowing the effective concentration of monomers tends to produce more spherical or isotropic particles, as the faster-growing facets do not have the high concentrations their rapid growth requires. This is simply a heuristic, however, and nuclei in material systems with tendencies to grow more anisotropically, like those with layered crystal lattices, tend to overcome concentration control.²⁰ Gold nanocrystals are one case where this does hold strongly, and syntheses that modulate the concentration of the ascorbic acid reducing agent can change the effective concentration of gold monomers.²¹ The addition of monomers either through a fast injection, or a slow drip also exemplifies this concentration control. While a fast injection of monomers pre-nucleation will cause rapid burst nucleation, a similar addition after the fact would produce polydisperse and possibly anisotropic particles. This is why the slow addition is preferred when layers are being grown onto the surface of nanocrystals, as is common with quantum dots.^{22,23}

Colloids

When the surfactants on the surface of a crystal prevents aggregation, and the particle is small enough that gravity is negligible, the particle will be suspended in the solution it nucleated in. This is an example of a colloid, or a mixture of one material dispersed in another. This is a wide reaching definition and it encompasses a large number of systems.²⁴ In this thesis, the only mixtures discussed are solid particles dispersed in liquid solvents. While the definition of a colloid does not address about how long-lived the dispersed phase is, to be colloidally stable is to be solvated within the solution at timescales that make it possible to treat the solution as a single phase. A stable colloid, often covered in surfactants that match the solvent, can remain suspended theoretically indefinitely if dilute enough such that no aggregation or flocculation can occur, yet practically speaking, colloids are only kinetically stable. The motion of colloids is discussed more thoroughly in subsection 2. Just like with monomeric addition, surfactants on the surface of a particle will preferentially bind to active sites and coordinate with the dangling bonds at the surface of the particle. This surface passivation slows down crystal growth on the facets coordinated by the ligands.

Ligands come in three basic types: two-electron donors (L-type), one-electron donors (X-type), and two-electron acceptors (Z-type). L-type ligands are commonly alkyl amines or alkenes. X-type ligands can be the halides, phosphonates and phosphinates, or carboxylates. Z-type ligands are typically Lewis acids like BF_3 or complexes between a metal and an L-type ligand like cadmium oleate.²⁵ Engineering the ratios of various ligands is a common technique in shape engineering. Alkyl amines and carboxylic acids are commonly used in this way, with oleylamine and oleic acid being the most famous.²⁶ Thiols and phosphines are also quite common.^{27,28} The specific binding modes and coordination strengths of the ligands on various crystal facets greatly affect the facet specific growth rates. For instance, alkyl ligands, which are used extensively in non-polar solvent systems, can be engineered with different lengths, tail densities, and saturation (number of double bonds in the carbon-carbon chain) to greatly tune the steric hindrance of monomers diffusing towards the surface.^{29,30}

Non-Classical Growth and Assembly

So far, the growth of spherical particles has been entirely predictable with classical growth mechanics involving the attachment of individual monomers. Mechanics such as this are a useful descriptor in most systems, but significant challenges and opportunities present themselves in systems where we deviate from the classical descriptions. While the definition of non-classical is, of course, anything that is not classically described, non-classical growth typically involves growth that uses or passes through an intermediate stage. Examples of this include oriented attachment where crystal building blocks attach on facets to produce a larger crystal,^{31–33} aggregation and coalescence,^{34–36} and reshaping through phase transitions among a host of others.^{37–39} Many cases also exist where multiple phenomena combine to produce entirely unique crystallization behavior.^{40–42} In Figure 2.4 a simplified map can be seen. This is not all-encompassing, and crystallization processes often do not cleanly follow a single path.

As a general class, aggregation is one of the most common non-classical mechanisms. There are a great many ways it can manifest, but it ultimately requires the transport of primary particles towards one another and the final attachment once they come into contact. This attachment can be random, or ordered which involves the alignment of crystallographic facets as previously mentioned. The final product of aggregative crystallization can be polycrystalline, mesocrystals (aggregates with crystallographic registry between

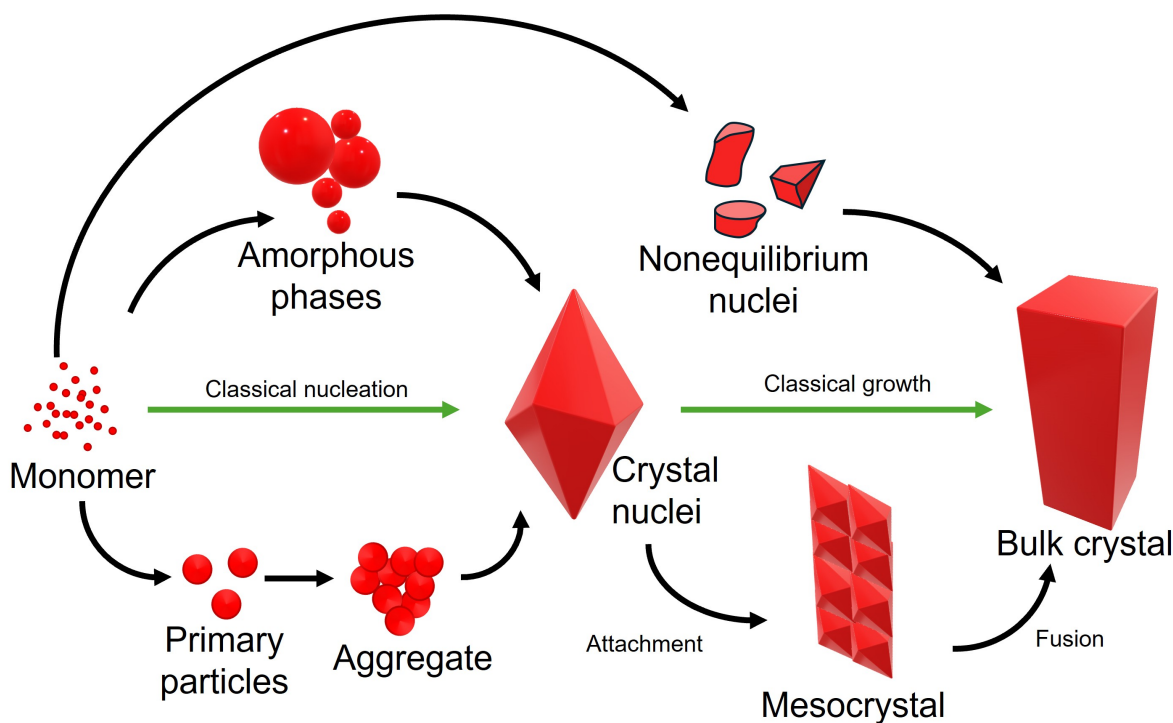


Figure 2.4: Figure depicting classical and a selection of non-classical nucleation and growth mechanisms.⁴³

the primary particles), or even pristine single crystals after internal restructuring.⁴⁴ Since aggregation requires that there be contact between primary particles, it can be mitigated using surface ligands, reducing the number concentration in the solution, or both simultaneously. Aggregation can be sped up then by ligand stripping, increasing the concentration, or increasing the number of collisions with vigorous stirring. Therefore, aggregation can often be an intentional and tunable phenomenon with the use of organic molecules to direct the assembly.

Directing assembly is an incredibly wide field that is used both to direct the crystallization process,⁴⁵ as well as to impart additional function onto primary particles.⁴⁶ Aggregation is the broader term, encompassing both ordered and unordered clustering, while assembly implies intentional or directed arrangement.⁴⁷ Nanoparticle assembly into stable structures is affected by the shape and morphology of the particles,⁴⁸ through the use of templates (e.g. patterned surfaces or self-assembling polymers),^{49,50} by surface bound ligands,⁵¹ by external fields,⁵² and registered crystallographic directions. With respect to crystallographic registry, this can be mediated either through the attachment of specific facets,⁵³ or by the facet-specific capping of ligands which can influence alignment of nanocrystals during packing.⁵⁴ Because of this, the

nanoparticle structure and morphology are strong predictors for highly ordered self-assembly in the absence of a template or external field. For example, large aspect ratio nanostructures pack into hexagonal arrays,^{55,56} and monodisperse spheres typically experience close packing into face-centered cubic or hexagonal close-packed lattices.^{57,58}

2.1.3 References

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2.2 Diffusion

2.2.1 Molecular Diffusion

The descriptions of diffusion are numerous and far reaching into a variety of disciplines. At its core, diffusion is the transport of a species through a medium driven from an area of high concentration to an area of low concentration. This manifests in a variety of different ways, but we’ll explore a select number of common and relevant cases in this chapter. To a chemist, perhaps the most quintessential case of diffusion is molecular diffusion through a liquid medium. One of the first mathematical descriptions of diffusion came from Adolf Fick in 1855 who built his description of diffusion phenomenologically using an experimental setup inspired by Thomas Graham’s earlier work on the diffusion of gases.¹ Fick’s laws of diffusion form

the basis for the transport of mass in solids, liquids, and gases. Fick's first law (Equation 2.7) relates the flux, or flow rate through a given area, to a concentration gradient where J is the diffusion flux, D is the diffusion coefficient or diffusivity with units of area per time, and $\frac{dC}{dx}$ is the concentration gradient.

$$J = -D \frac{dC}{dx} \quad (2.7)$$

Fick's first law assumes an ideal and dilute solution, where the diffusing species does not experience any interaction with itself or another species (infinitely dilute) and is time independent. The diffusion medium is assumed to be isotropic and the species is assumed to have a constant diffusion coefficient. Together, this makes Fick's first law most applicable for dilute solutions of binary mixtures where molecular interactions and concentration gradients are low.

In his same paper, Fick described a conservation of mass (Eq. 2.8, Fick's second law) where the time evolution of a concentration gradient follows a partial differential equation where $\frac{\partial C}{\partial t}$ is the derivative of the concentration (C) with respect to time (t), and $\frac{\partial^2 C}{\partial x^2}$ is the second derivative of the concentration with respect to position (x). The diffusivity remains D with the same units. This equation is identical to the heat equation in one dimension, when all other forms of transport other than diffusion are neglected, and the solution follows the same form (Eq. 2.9)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2.8)$$

$$C(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (2.9)$$

In the case where the rate of diffusion is not constant with respect to position, Fick's second law takes the form

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (2.10)$$

By integrating Fick's second law of diffusion with respect to space and then time, the result is a useful equation relating the position to time with the diffusion constant. This is known as the mean-square displacement (Eq. 2.11).

$$\langle x^2 \rangle = 2Dt \quad (2.11)$$

Fick's second law follows from his first through the partial differential equation for the conservation of

species, and the same assumption of a dilute and ideal solution applies. In nonideal cases where the interaction between species is non-negligible, as is the case with multicomponent systems, the Maxwell-Stefan equations predict diffusion more rigorously.² The Maxwell-Stefan equations are based on the assumption that the diffusion of a species through a medium will coincide with a balance between the concentration gradient and the friction that the species experience as they interact with one another. The theory relies on the activity and gradient of chemical potential, rather than concentration, as the driving force for the various molar fractions of species. It follows that the Maxwell-Stefan diffusivities depend on the makeup and interactions within the system and are not substitutable with Fick's diffusivities (unless under ideal, dilute conditions where Maxwell-Stefan and Fick's laws converge).³

But Fick's laws and the Maxwell-Stefan equations operate within a continuum, or, the average behavior of many particles. The equations they built were influenced by the bulk phenomena they witnessed. Absent from their derivations was a fundamental explanation of *why* species traveled against a concentration gradient. The reality is that the phenomena they witnessed emerged from the random motion of many individual species. At shorter length scales, where the motion of individual particles becomes non-negligible, a different model is required that relates random motion to average displacement. Interestingly, the random motion of tiny particles was discovered much earlier, predating even Fick's or Graham's work, in 1827 by botanist Robert Brown when he observed the chaotic movement of pollen on the surface of water.⁴ We now describe this as Brownian motion. This motion results in a particle in solution following a meandering path, or 'random walk', that is driven by thermal energy and collisions between particles. Figure 2.5A shows a simulation on a 2D plane of this random walk for 100,000 particles that began at the origin and took 150 individual steps. Of the 100,000 particles, 1,000 paths were plotted in gray and 6 were given color to illustrate their motion.

The displacement of each particle from the origin, which can be positive or negative, follows a normal, or Gaussian, distribution. However, the total distance each particle traveled from the origin, which is a positive value, follows a Rayleigh distribution (in three dimensions this is called a Maxwell-Boltzmann distribution). As the simulation progresses, the particles would inherently travel further from the origin and the full-width-half-max of the distribution would increase. Since the particles are in a 2D plane, we can calculate the distance from the origin using the trigonometric relation $r = \sqrt{x^2 + y^2}$. This radial distance (Figure 2.5B)

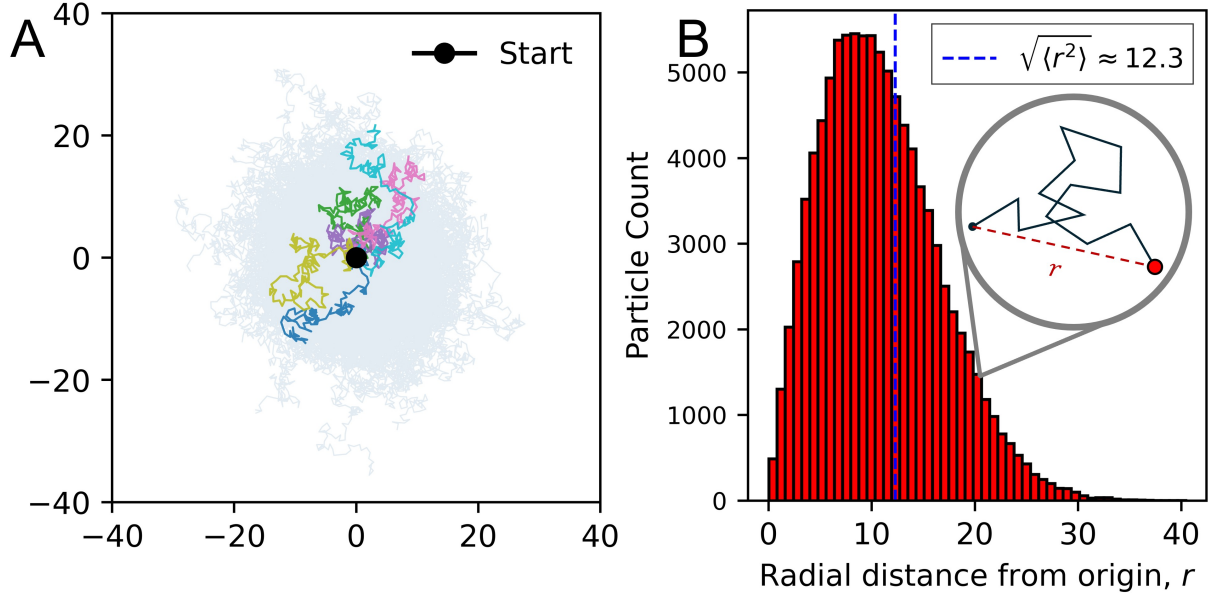


Figure 2.5: **A)** A 2D plane plotting the paths of 1,000 random particles from a set of 100,000 experiencing a random walk (150 steps, step size of 1). A random six paths were colored out of the 1,000 in gray. **B)** A histogram plotting the displacement, $\langle x^2 \rangle$, from the starting point of 100,000 individual particles. Root-mean-square-displacement, $\sqrt{\langle r^2 \rangle}$, was calculated using an ensemble average and marked with a blue line. Inside the gray circle illustrates the definition of radial distance, r , for a single example particle following a random walk.

follows a Rayleigh distribution as it is non-negative. The root-mean-square-displacement, or the ensemble average of distance traveled, can be calculated from the distribution with equation Equation 2.12.

$$\langle r^2 \rangle = \frac{1}{N} \sum_{i=1}^N (x_i^2 + y_i^2) \quad (2.12)$$

In the case of the simulation in Figure 2.5, this mean-square displacement is approximately 12.3 given a step size of 1 (arbitrary units). Given a large number of particles, this diffusion can be treated using continuum mechanics. This is ultimately the fundamental stochastic phenomenon driving the bulk diffusion that Fick and Graham witnessed.

The theory that achieves the marriage of the statistical mechanics that describes Brownian motion and bulk transport was developed separately and simultaneously by Einstein (1905) and Smoluchowski (1906). To simplify the notation, we'll consider the 1-dimensional case of a particle that moves back and forth along a line in step sizes of δ at time intervals of τ . It has equal probability of moving to the left or moving to the

right. After N steps, the position (x) is the sum of all of its steps. This can be expressed mathematically as the following:

$$x_N = \sum_{i=1}^N \pm \delta \quad (2.13)$$

Since the particle has an equal chance of moving left and right, the average distance it will travel is zero ($\langle x_N \rangle = 0$). Where $\xi_i = \pm \delta$, the full expression is the following:

$$\langle x_N^2 \rangle = \left\langle \left(\sum_i \xi_i \right)^2 \right\rangle = \sum_i \langle \xi_i^2 \rangle + 2 \sum_{i < j} \langle \xi_i \xi_j \rangle = N \delta^2 \quad (2.14)$$

where the cross terms vanish because successive steps are independent. We substitute $N = t/\tau$, and if we define diffusivity as $D \equiv \delta^2/(2\tau)$ then the final form matches the mean square displacement derived from Fick's law.

$$\langle x^2 \rangle = N \delta^2 = \frac{\delta^2}{\tau} t = 2Dt \quad (2.15)$$

2.2.2 Colloidal Diffusion

Particles that are a different phase than the surrounding solution they are suspended in are known as colloids (discussed in subsection 2). If the colloids are stable, meaning over relevant timescales they behave as if they are solvated, they largely obey the same fundamental behavior of diffusion. However, since colloidal particles are often at least one or two orders of magnitude larger than molecules, their interaction with the surrounding solvent approaches continuum mechanics. Their greater mass also makes gravity non-negligible in their motion, and their larger size and ligand-coated surface create significant interparticle interactions. In this section, these phenomena will be introduced, but should a deeper explanation be desired, the textbook titled *An Introduction to Interfaces and Colloids* by Berg is an excellent practical resource.⁵

For a molecule of comparable size to the medium around it (on the order of angstroms), its diffusion can be quite rapid compared to a colloidal particle (on the order of nanometers and microns). Independently arrived at by Sutherland,⁶ Einstein,⁷ and Smoluchowski,⁸ the relation between kinetic energy, mobility, and the diffusion coefficient can illustrate the difference. In this form (Equation 2.16), k_B is the Boltzmann

constant, T is the absolute temperature, and f is the friction coefficient, or drag, the particle experiences.

$$D = \frac{k_B T}{f} \quad (2.16)$$

If we assume a spherical particle moving through a viscous fluid, we can substitute the friction coefficient using Stokes' law, $f = 6\pi\eta r$, to arrive at the Stokes-Einstein equation.⁹

$$D = \frac{k_B T}{6\pi\eta r_H} \quad (2.17)$$

In Stokes' law, η is the dynamic viscosity of the fluid, and r is the radius of the particle. When we consider the radius of a colloid, or rather any particle moving through a liquid medium, the particle drags along with it a number of water molecules that surround it in a hydration sphere. This is why the radius of particles effectively appears larger than the solid itself when measured,^{5,10-13} and it is why the hydration radius, r_H , is used in Equation 2.17.

Using Equation 2.17, it is apparent that the diffusivity of a particle is inversely proportional to the radius ($D \propto 1/r$). An aqueous Co^{2+} ion, for instance, which coordinates with 6 water molecules ($[\text{Co}(\text{H}_2\text{O})_6]^{2+}$) to form a core hydration shell of ~0.21 nm and a full hydrodynamic shell of 0.41-0.43 nm,¹⁴ has a calculated diffusivity of $5.18 \times 10^{-10} \text{ m}^2/\text{s}$. For comparison, casein micelles (one of the protein aggregates found in milk) range in size from 100 to 300 nm.¹⁵ They would have a calculated diffusivity (when infinitely dilute) of $\sim 1.45 \times 10^{-12} \text{ m}^2/\text{s}$. At equal concentrations then, the velocity of the cobalt ion would be 100 times greater than that of the casein micelle. The behavior of a colloid diffusing through water molecules is more akin to "a blimp being bombarded with basketballs",⁵ and is why the diffusion coefficient of colloids is best measured with scattering techniques rather than bulk flow observations.

Given that the size of colloids is typically orders of magnitude larger than ions and molecules, the effects of gravity are non-negligible. A particle in a solution is constantly battling the force of gravity with two competing forces: 1) Brownian motion and 2) buoyancy. A force balance of gravity and buoyancy on a particle results in Equation 2.18 where the difference in density of the particle (ρ_p) and the fluid (ρ_f)

multiplied by the acceleration due to gravity (g) results in either the particle floating ($+F_g$) or settling ($-F_g$).

$$F_g = 4/3\pi r^3(\rho_p - \rho_f)g \quad (2.18)$$

A force balance of F_g with the Stokes drag that the particle experience from the surrounding fluid results in the sedimentation velocity, Equation 2.19.

$$v_s = \frac{2r^2(\rho_p - \rho_f)g}{9\eta} \quad (2.19)$$

The competition between the gravitational settling force, F_g , and Brownian motion determines whether or not a colloid will settle. The Péclet number is a dimensionless number that compares this Brownian motion and gravitational settling using the sedimentation velocity and the diffusion coefficient (Equation 2.20).

$$Pe = \frac{v_s r}{D} = \frac{\text{Sedimentative Transport}}{\text{Diffusive Transport}} \quad (2.20)$$

A Péclet number greater than 1 indicates that the particle will sediment, while less than 1 might indicate that the size of the particle is small enough that Brownian motion can keep it suspended. This is only considering a case where the colloids are dilute enough, or repel one another sufficiently, that no aggregation occurs. Should colloids aggregate, then the effective size quickly becomes much larger, and sedimentation can occur. This makes flocculation and sedimentation an efficient separation technique for removing colloids from solution. It is also an effective purification technique to size-selectively centrifuge the largest particles out of solution while keeping the smallest suspended.^{16–18} This flocculation can either be engineered or inherent to the system itself. Assembly and interparticle forces are discussed in more detail in subsection 2.

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2.3 Hydrogels

Hydrogels are a class of materials that consist of hydrophilic polymers that form a cross-linked 3D network. There are a wide number of materials that roughly fit this description, which vary greatly in the chemical structure of the polymer backbone, functional groups, and the type and degree of cross-linking. What they demonstrably have in common is that a hydrogel, by mass, is mostly water, and it retains its structure through its network of bonds. Though it is possible to prepare a hydrogel with water content as little as 10% or less,¹ most hydrogels are at least 50% water, and some even exceed 99% water.² Hydrogels are usually described by the weight percentage of the gelling agent used in a given volume of water. It is common, however, for the volume of the gel to change as hydrogels are dynamic structures. They swell with water, shrink as they dry, and some can even respond to stimuli in the environment such as pH, salt content, and temperature, which modulates their structure and the amount of water they absorb.³ Some gels are so sensitive to certain stimuli that they can be engineered for advanced applications in biomedical fields,^{4–6} microfluidics,⁷ and even wastewater treatment, among many others.⁸

Hydrogels are predominantly characterized by their structure in a swollen state. This topological structure is fundamentally tied to the molecular structure of the polymer backbone as well as the method of polymerization, crosslinking, or both. The structure of gels is rarely uniform as defects exist across multiple length scales. At the smallest scale, polymer strands can dangle into the network without a bonded termination, which makes them elastically inactive as they will not support stress.⁹ Two of the more significant structural parameters for a gel are the mesh and macropore sizes. The mesh size is the average distance

between polymer strands or domains and typically has a wide size range from a few nanometers to many tens or hundreds of nanometers.¹⁰ This is because there are both spaces between polymers, on length scales of 1-10 nm, as well as spaces between dense regions of polymers, on length scales of 10-100 nm or even beyond. Examples of these can be seen in Figure 2.6. Macropores are much larger, typically many micrometers in size and outside the range of most scattering measurements. The mesh size is typically measurable using scattering techniques and can refer to both the polymer and domain spacing depending on the model used to describe the gel. The mesh size is strongly related to the correlation length, ξ , which is the average distance between segments of polymers (Figure 2.6).

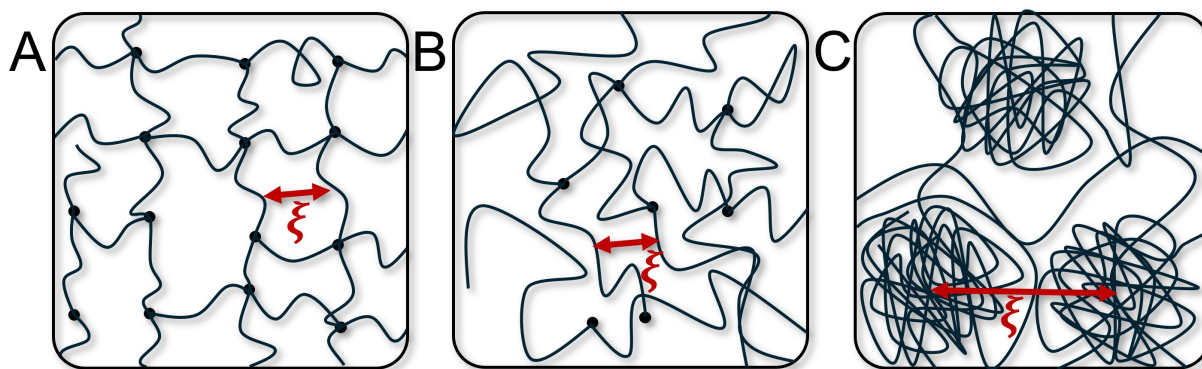


Figure 2.6: Graphic depicting hydrogels that have **A)** a regular characteristic length, ξ , prepared from end-to-end linking of polymers with a suitable linker, **B)** an irregular characteristic length prepared from the random crosslinking of polymers, and **C)** a regular characteristic length from the uncontrolled chain growth crosslinking of polymers resulting in inhomogeneities. The red arrows indicate where the characteristic lengths originate.

The characteristic length in and of itself is an imperfect descriptor of hydrogel structure for this reason. When measured directly with scattering, the characteristic length can be attributed to regular spacings between highly ordered polymeric lattices (Figure 2.6A), average spacing between disordered polymer chains (Figure 2.6B), or average spacing between denser regions of polymer (Figure 2.6C). The lack of structural clarity it provides means that multiple modes of measurement need to be made to determine the topological structure of a hydrogel, along with inherent chemical knowledge of the polymer and its preparation. Scattering measurements to determine a characteristic length will be discussed in more detail in subsection 3.

To achieve the most complete understanding of hydrogel structure then multiple characterization techniques across length scales are required.⁹ Proton NMR and spectroscopies like FTIR and Raman can in-

investigate the structure of the polymer itself, while scattering and macro scale measurements on the bulk properties like the swelling and modulus can, through theory, be used to calculate mesh size.¹¹ However, it will always be required to understand the fundamental chemistry behind the crosslinking and polymerization to make accurate assumptions. In Figure 2.6, there are three cases where this becomes important. In Figure 2.6A, the hydrogel is prepared via polymers and a linker to create a regular network. Figure 2.6B shows polymers that randomly link end-to-end to produce a wide range of characteristic lengths. Finally, Figure 2.6C shows a similar case to the previous, but the polymer forms inhomogeneities. These manifest across multiple length scales, as is common with random orientation.¹²

2.3.1 Properties and Structures of Relevant Gels

The number of hydrogels is effectively as numerous as there are molecular arrangements of water-soluble polymers. We will focus on a select number for this brief review that are relevant to the work within this thesis. The three hydrogels discussed in this section represent three broad types of hydrogels: natural and non-covalently linked (agarose), polymeric with end-to-end attachment (PEGDA), and those that are monomerically polymerized (polyacrylamide).

Poly(ethylene glycol) diacrylate

Poly(ethylene glycol) diacrylate, or PEGDA, is a synthetic hydrogel that is extensively used in biomedical applications due to its biocompatibility.¹³ Some of the bulk properties of PEGDA are tunable by changing the length of the ethylene glycol backbone. PEGDAs are often sold by molecular weight, with 250, 500, 700, 4k, 10k, and 20k g/mol all readily available from vendors. As an aside, 700 Mw PEGDA is the most common and is a liquid at room temperature, making it easy to manipulate. Higher molecular weights will be more specialized and a solid at room temp. Changing the length of the PEGDA changes the elasticity of the structure, as well as the solubility of polar species, since higher molecular weights have longer ethylene glycol chains and are more water soluble. The shorter PEGDAs have a higher concentration of acrylate groups, which are less polar when covalently linked.

There are multiple avenues to preparing PEGDA into a gel, which involve the generation of free radicals either with a chemical initiator like TEMED (N,N,N',N'-tetramethylethylenediamine) or a photoinitia-

tor like LAP (Lithium phenyl-2,4,6-trimethylbenzoylphosphinate). When polymerized, PEGDA undergoes chain growth where the diacrylate ends of the PEGDA chains link onto one another as the free radicals propagate. Since the poly(ethylene glycol) backbones do not typically participate in crosslinking, the diacrylate forms this 'bottle-brush' structure where rigid polymerized acrylate is surrounded by long PEG chains.¹⁴ There are effectively multiple characteristic length scales then: the spacing between the polymer chains (0.1 - 5 nm), the spacing between rigid acrylate bottle brush structures (3 - 8 nm, d in Figure 2.7), and the macropores that are on the micrometer scale (Figure 2.7). Figure 2.7 shows the molecular structure and how it leads to this bottle brush formation where the red circles denote the acrylate ends of the PEGDA. The radius of gyration (R_g) is also shown, which is commonly modeled in scattering measurements as the size of the densely crosslinked domains.

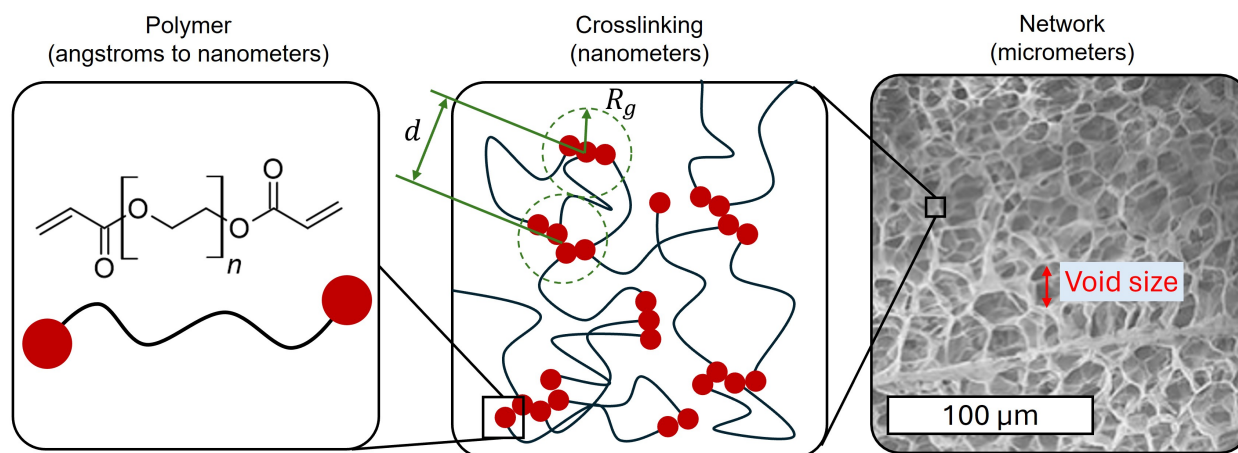


Figure 2.7: Chemical structure of poly(ethylene glycol) diacrylate and the structure after crosslinking. The distance d is the characteristic length, sometimes referred to as ξ , and the domain size is the radius of gyration, R_g , of the densely crosslinked domains. The overall network of macropores is shown in a cryo SEM image of a 10k Mw PEGDA hydrogel from Lin *et al.*, licensed under CC BY-NC 4.0.¹⁵ Based on hydrogel structures from Rahman *et al.*,¹⁶ licensed under CC BY 4.0.

As is the case with many hydrogels, the structure of the PEGDA is tunable. There are two main handles with PEGDA: the weight fraction and the length of the chain. The largest change is had when the weight fraction is modulated. Lower weight fractions (5 to 10 wt%) necessarily space out the polymer more and result in larger mesh sizes (characteristic lengths, ξ), while increasing the weight fraction results in a more uniform structure with smaller mesh sizes.¹⁷ Depending on the molecular weight, the lowest possible weight fraction will be around 5 wt% which will increase with higher molecular weights as the molar fraction of

polymerizable acrylate groups in a solution decreases as PEGDA molecular weight increases.

Polyacrylamide

Polyacrylamide (PAA) is another synthetic hydrogel system based off of polymerized monomers of acrylamide crosslinked with a species like methylene bisacrylamide (BisAAM). The initiation of the polymerization can be done identically to PEGDA, using free radical generators like TEMED or LAP. Unlike PEGDA, however, polyacrylamide is polymerized from monomers, not chains. This makes the chain length and network density more dependent on the concentration of the initiator. Increasing the concentration of the initiator increases the number of sites where polymerization begins, which reduces the polymer length. In some cases, the polymers can become so short that they remain dispersed in solution, and a 3D network cannot occur.¹⁸ The total weight fraction of a polyacrylamide hydrogel is very similar to PEGDA, but increasing the weight fraction tends to make the gel more rigid much quicker than PEGDA. The structure is also more uniform than PEGDA at every weight fraction, as no bottle brush structures form. This is why PAA is used frequently for electrophoresis, as the mesh size is highly regular and able to resolve small differences between molecules.¹⁹

Like PEGDA, there are multiple length scales to consider within a crosslinked polyacrylamide hydrogel. Figure 2.8 breaks these length scales into 4 discrete regions; however, it is important to understand that these four regions overlap significantly with one another.²⁰ The shortest lengths are the crosslinkers themselves, which are approximately 0.2 nm in length. These crosslinked regions can form clusters that are approximately 1 to 10 nm in size. The distance from one domain to another is the characteristic length, or mesh size, and can vary from 10 nm to up to a micrometer.²⁰ These domains make up the macroporous network, which has voids many tens or hundreds of micrometers large.

The mesh size is highly tunable in PAA gels. This is because the crosslinker functions as an additional handle for tuning the characteristic spacing between polymer strands. Researchers measured a characteristic length that was tunable from 1.4 to 7.5 nm by adjusting the weight fraction of a BisAAM (N,N'-methylene bisacrylamide) crosslinker from 1 to 9 wt%.²¹ This, combined with changing the identity of the crosslinker, makes for a wide parameter space that is structurally tunable.²² Figure 2.8 Shows the product of the polymerization and crosslinking of acrylamide with BisAAM in a reaction with an initiator.

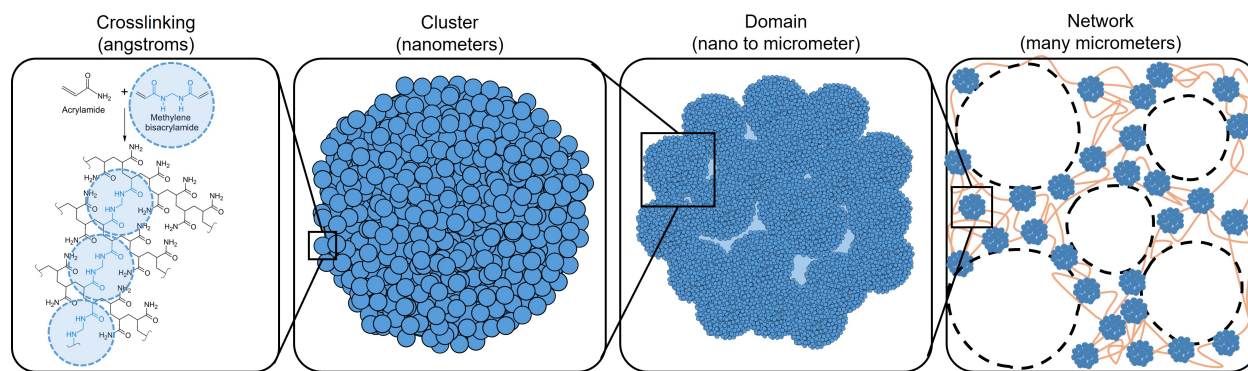


Figure 2.8: Chemical structure of polyacrylamide and the crosslinker methylene bisacrylamide with the final structure after polymerization. The blue spheres represent the regions bridged by a crosslinker, while the orange strands represent un-crosslinked polyacrylamide. Based on the hydrogel structure from Gombert *et al.*,²⁰ licensed under CC BY-NC 3.0.

Agarose

Agarose is a naturally occurring polysaccharide that is purified from marine red algae, where it is separated from the agaropeptin in agar. It is most famously used for gel electrophoresis,²³ where it's used to separate DNA fragments and proteins by size. However, its selectivity is poorer than hydrogels with a finer mesh size, such as PAA. The structure of agarose results from its supercoiled structure of helices that form 20-30 nm thick bundles (Figure 2.9).²⁴ These bundles then assemble into a network with large macropores on the order of a micron. The result is three distinct size regimes: the distance between the polymer chains, the sizes of the helical bundles, and the distance between the helical bundles that form macropores. There is a large tunable range for the macropores, which can vary from 0.1 to 1.2 micrometers.²⁵ Unlike the covalently bound synthetic gels, agarose polymers link via hydrogen bonding. The molecular structure of agarose and the multiple hydrogen-bonding-capable hydroxyl groups can be seen in Figure 2.9. The gel is prepared by heating an aqueous solution of agarose between 90 and 100°C before allowing it to cool, which results in a more inhomogeneous gel depending on the rate of cooling and geometry of the container. The hydrogen bonding is also susceptible to disruption during reheating. These helices are both long and extremely rigid, making it possible to prepare agarose gels with weight percents as low as 0.3 wt%, though 0.5 to 2 wt% are most common.²⁶

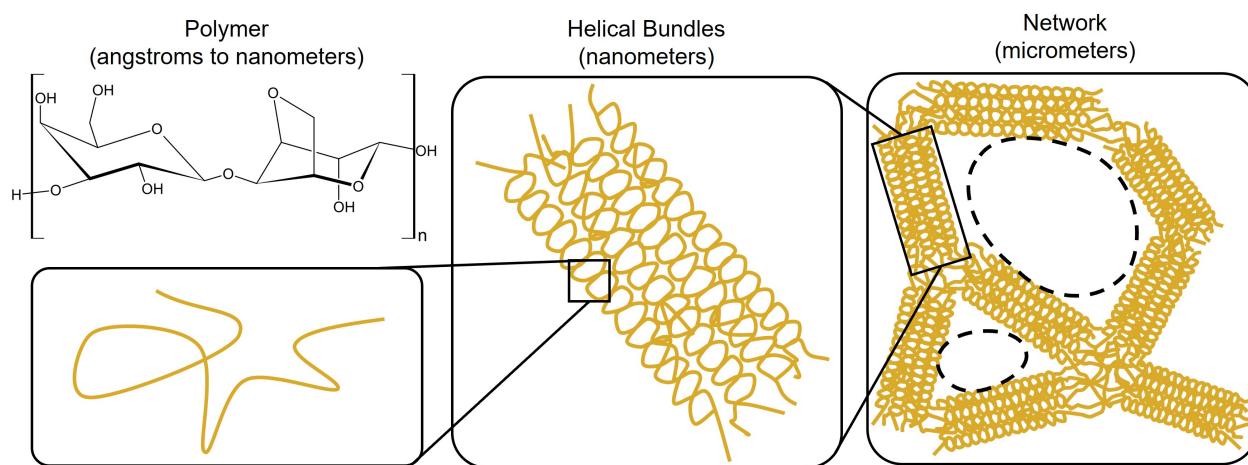


Figure 2.9: Chemical structure of agarose, a disaccharide comprised of D-galactose and 3,6-anhydro-L-galactopyranose. Hydrogel structure from Zarrintaj *et al.*,²⁷ licensed under CC BY 4.0.

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2.4 Reaction-Diffusion Coupling

2.4.1 Defining the Coupling

Reaction-diffusion coupling combines the established and well-understood problems of reaction mechanics and diffusion to create a complex field of study which quickly results in far-from-equilibrium, nonlinear,

phenomena. As the molecular diffusion of species influence their reactions and vice versa, complex patterns and reaction products spontaneously emerge over both space and time. These phenomena emerge when the rates of diffusion and reactivity are both non-negligible considerations that create a close dependency where the reaction shapes the concentration field while diffusion removes and resupplies reagents. One of the earliest reaction-diffusion phenomena that was described, and likely became the most quintessential, was periodic precipitation. This was first described by chemist Friedlieb Ferdinand Runge in 1855 in his book titled "*The Formative Tendency of Substances, Illustrated by Autonomously Developed Images*" (Der Bildungstrieb der Stoffe, Veranschaulicht in Selbstständig Gewachsenen Bilder, trans.) with his observations of reactions on blotting paper.¹ Later, Raphael Liesegang, for whom the phenomena is more widely attributed to, would notice a similar autonomous phenomena in gels in 1896.² Figure 2.10 shows an example of a Runge blot prepared using cobalt (II) chloride impregnated filter paper and drops of dibasic potassium phosphate and sodium hydroxide. The white concentric rings illustrate the depletion effect where cobalt in the filter paper diffused towards the sodium hydroxide or potassium phosphate before reacting.

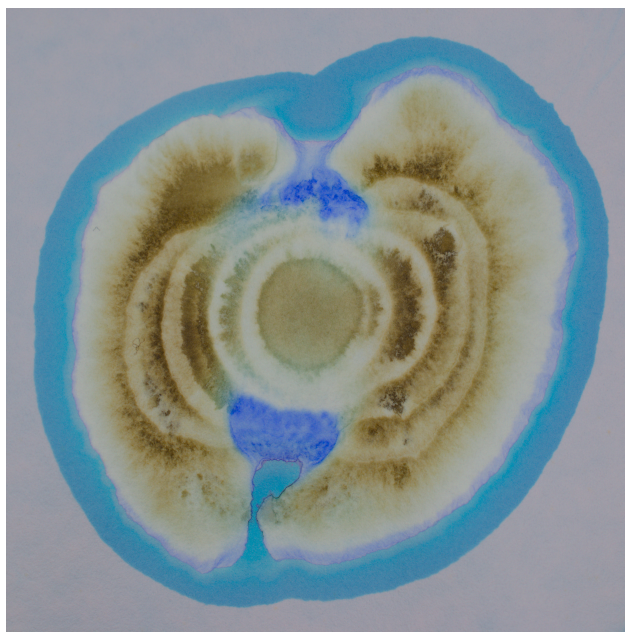


Figure 2.10: Runge blot made of filter paper first covered with 1 M cobalt (II) chloride then allowed to partially dry. Drops of dibasic potassium phosphate (2 M) then sodium hydroxide (2 M) were added to the center of the filter paper, allowing the filter paper to dry between additions.

In Liesegang's gel system, the diffusion of a solution of silver nitrate into a gel containing potassium

dichromate produced autonomously organizing concentric rings of insoluble silver dichromate. Often times, in this and many other systems, the solution outside the porous medium is called the outer electrolyte, while the solution inside the medium is called the inner electrolyte. Periodic precipitation also shows up in the field of geology where periodic precipitation results in banding seen in permeable igneous and metamorphic rocks.³ A related phenomenon are Turing patterns, found in vegetation patterns, animal coat markings, as well as in gel reactors in a lab setting.⁴⁻⁶ Chemical waves are another subset of reaction-diffusion phenomena, with traveling oxidation fronts found in inorganic systems and calcium waves found in neurons.⁷⁻⁹ Reaction-diffusion phenomenon can be found everywhere there is transport and a chemical reaction.

Reaction-diffusion coupling is described by the diffusion equation with an added reaction term for the generation or consumption of each species in the system. In the 1D reaction-diffusion equation (Equation 2.21), D_i and C_i are the diffusion coefficient and concentration of the i th components, respectively. $R_i(C_1, C_2, \dots, C_n)$ is the reaction term which depends on the concentration of the reacting components.

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + R_i(C_1, C_2, \dots, C_n) \quad (2.21)$$

In subsection 2, we discussed the theory of diffusion and the origins of molecular motion. This transport phenomena is relatively simple compared to the complexity of the reaction term which can vary greatly in its nature depending on the reaction it models. After all, diffusion is described with a linear partial differential equation with necessarily smooth solutions. Reaction-diffusion is described by non-linear partial differential equations which often are instable. There is a library of reaction types that are of importance to reaction-diffusion coupling including autocatalytic, characterized by a product that catalyzes the reaction;¹⁰⁻¹² bistable, where two stable products are separated by an unstable one;^{13,14} excitable media, where a single rest state can be perturbed before it settles back to rest;^{8,15} and oscillatory, where the reaction cycles between states autonomously.^{16,17} There are also additional complexities that can develop by adjusting the directionality of the flux. Whether the outer electrolyte flux is unidirectional or bidirectional has significant impact.¹⁸

Despite a vast reaction-diffusion space, there are fundamental descriptors of behavior that we can rely on to predict behavior. Reaction type is one, and the Damköhler number (Da) is another. The Damköhler number is a dimensionless number that is defined by the ratio of the reaction timescale to the transport

timescale (Equation 2.22) where τ is the timescale, k is a first order reaction constant, L is a characteristic length, and D is a diffusion coefficient. The form that this takes can change depending on the system, but most reaction-diffusion processes follow this structure.

$$\text{Da} = \frac{\tau_{\text{diffusion}}}{\tau_{\text{Reaction}}} = \frac{kL^2}{D} \quad (2.22)$$

The Damköhler number describes the balance of the reaction and diffusion rates which are responsible for directing the morphology of autonomous organization,^{19,20} as well as any reaction products that form as a result.²¹ A significant consideration worth mentioning with the Damköhler number is that the diffusivity as it is presented here is an effective diffusion coefficient, not a literature molecular diffusivity. This is because the literature value is only applicable within the assumptions made by Fick's law, an ideal dilute case. This was described more thoroughly in subsection 2. Reaction-diffusion systems rarely operate within ideality, oftentimes having high concentrations and significant molecular interactions with the surrounding media, whether that be a gel or viscous fluid, with a great deal of functional groups. Additionally, the reaction kinetic term is only valid for one-step reactions of the form $A + B \longrightarrow C$, $A + A \longrightarrow B$, or similar. It is also exceedingly common for non-idealities to develop over length and time scales not captured in the linear mechanics of the Damköhler number. Nonlinear physics like supersaturation thresholds, or even the vast number of non-classical crystallization reactions,²² can exhibit completely different behavior, making the Damköhler number more useful for comparisons within systems rather than across them.

2.4.2 Porous Media in Reaction-Diffusion

Possibly one of the most important aspects of a reaction-diffusion system is the media that the transport and chemistry occur in. Over the shortest length or time scales, reaction-diffusion phenomena can develop at the surface of any solid, such as catalysts,^{23,24} channels,²⁵ or across surfaces and thin films.²⁶ For longer lengths and time scales, however, it is absolutely critical that convection or other forms of mixing be negligible. The type of media that best supports this are porous solids like gels or certain rock.^{27,28} In most lab settings, hydrogels are the most commonly employed medium to fit this purpose. Hydrogels are discussed in more detail in subsection 2, but their relationship with reaction-diffusion phenomena will be introduced in this section.

The number of hydrogels used for reaction-diffusion work is as numerous as the number of chemistries; however, most research confines itself to a select number. Of the natural gels, agar (or refined agarose),^{29–31} gelatin,^{32,33} chitosan,³⁴ and alginate are common.^{35,36} Synthetic gels that are used are poly(vinyl alcohol),^{37,38} polyacrylamide,³⁹ or in the cases where biocompatibility is desired, polyethylene glycol.⁴⁰ In most cases, there is no methodological reasoning that motivates the selection of one gel over another beyond aligning the gel properties with an eventual application. Almost every reaction-diffusion system is sensitive to the gel structure, however, but studying this is incredibly challenging. Some studies have investigated the effect of the gel on reaction-diffusion phenomena, which include varying the gel density,⁴¹ composition,⁴² and even the thickness.⁴³ No systematic study, however, has taken place between disparate gel types that forms a causal link between reaction-diffusion phenomena and fundamental gel chemistry.

2.4.3 Opportunities and Challenges

Patterning

Research that utilizes reaction-diffusion phenomena to achieve a certain outcome focuses largely on two aspects: shaping the macroscale self-organized structure, or directing the reaction product itself. For controlling reaction-diffusion patterns, one of the most promising applications is advanced manufacturing that can produce structures that we would otherwise struggle to create. For instance, we currently dedicate massive clean-room fabrication facilities to the production of nano- and micro-scale architectures using lithography.⁴⁴ While incredibly powerful, lithography has limitations. One of the most significant being its scalability, which scales proportional to area. The field size, or maximum area that an exposure can print onto a substrate, is less than 900 square millimeters.⁴⁵ It is also limited to working on flat substrates. To reaction-diffusion patterning, however, area is a non-factor, and curved surfaces are easily achievable. As a manufacturing technique, reaction-diffusion could open the door to roll-to-roll printing of optical devices or other expensive components traditionally manufactured with lithography. Groups are already showing excellent control in this area. Van Campenhout *et al.* demonstrate controlling Liesegang bands with immersion dipping to produce regular wafer-scale lines and patterns that can function as diffraction grating.⁴⁶ The Grzybowski group has also demonstrated impressive pattern formations on many gel surfaces and volumes that are nearly arbitrary in how they are structured. Their method of 'wet stamping' has produced gratings,⁴⁷

microlens arrays,⁴⁸ and other advanced architectures.^{49,50}

Biological Mimicry

With reaction-diffusion, we can also aspire to the level of control over self-organization of biological systems. Morphogenesis is the process by which living things construct their shape. While biology might direct the formation of shells, patterns, and tissue through evolved chemical signaling and coordination, reaction-diffusion can produce similarly complex structures. Noorduin *et al.* demonstrate this level of control by producing a wealth of biologically inspired structures by initiating and modulating the diffusion limited growth of silica and carbonate.⁵¹ Resembling flowers, shells, and spirals, the precipitates are dynamically sculpted throughout the reaction-diffusion process by controlling pH and reagent concentration. Some similar structures were achieved from a naturally sourced alkaline water sample by Garcia-Ruiz *et al.*⁵² Besides leveraging this behavior for synthesis, it can also be used for preparing model systems to understand the fundamental driving forces of morphogenesis. Simplifying a biological system to a reaction-diffusion reactor can help unlock the fundamental driving forces of biomineralization 'one amino acid at a time',⁵³ or create defined vasculature-like structures by balancing diffusing and inhibiting species.⁵⁴

Crystallization

Since Runge and Liesegang described their rings in the mid-19th century, self-organized patterns have sparked a great deal of interest. However, leveraging reaction-diffusion to produce a specific product far from equilibrium has captured attention as well. The earliest example of reaction-diffusion coupling to produce a precipitate were gold crystals synthesized by Emil Hatshek in 1912 via the diffusion of oxalic acid through a silica gel loaded with gold chloride.⁵⁵ This was later generalized to other systems by Harry Holmes in 1917.⁵⁶ Some of the earliest industrial deployments of reaction–diffusion coupling for chemical production were immobilized-enzyme reactors, in which a porous gel or resin matrix fixed the enzyme in place while substrates and products diffused in and out of a flowing stream.⁵⁷ More modern examples of crystallization using reaction-diffusion coupling have identified the great utility that it can provide in precipitation reactions. One interesting case is employing gels to mimic the crystallization behavior inside the human body. Diseases like urolithiasis, arthritis, pancreatitis, atherosclerosis, cholelithiasis, and gout

can all involve biomineralization within the body, and gels offer a system highly amenable to studying the conditions where these crystallizations occur.³⁵

Likely the most important aspect of crystal production via reaction-diffusion coupling in gels, however, is not the biocompatibility of the media but the spatial encoding of reaction products. Many researchers note the incredible tunability of reaction-diffusion syntheses in gels as the products are spatially separated throughout the gel due to the continuously varying supersaturation conditions in the gel.⁵⁸ One such example comes from Damacet *et al.* who demonstrate this tunability during the synthesis of nickel and hexahydroxytriphenylene 2D MOFs (metal organic frameworks).⁵⁹ These 2D MOFs are tunable spatially throughout the column of gel because of the dynamic concentration gradient that develops. The result is that each position along the direction of diffusion in the gel experiences a unique concentration history and produces a unique crystallization product. While in the case of the gel, the concentration history is beholden to the effective diffusion coefficients of the reagents. In some cases, however, the rate of diffusion can be controlled. Yang *et al.* demonstrate a method of controlling the rate of transport of silver nitrate towards an electrode with a dynamic electric field. By controlling the pulse frequency and voltage, they are able to quantitatively adjust the Damköhler number on the fly to shape the growth of silver on a surface in a viscous solvent.^{60,61} While electrochemists often appreciate the reaction-diffusion coupling in their field, it's rarely discussed in the same breath as other reaction-diffusion phenomena despite the fundamental similarities. The dynamic formation of fractals illustrates how fundamentally the handles to controlling reaction-diffusion phenomena are the same across fields.^{62,63}

Separations

Most recently, reaction-diffusion has been demonstrated to be a potentially useful tool for separative technologies as well. Diffusive transport has long been a tool in the antisolvent-assisted crystallization of species,⁶⁴ demonstrated routinely in interfacial liquid-liquid separations and other systems where diffusive transport dominates.⁶⁵ Utilizing a precipitation reaction to achieve a similar separation is a novel concept that has recently been explored by researchers like Elias Nakouzi at the Pacific Northwest National Laboratory. Nakouzi and coworkers have demonstrated enhanced selectivity in the extraction of critical materials in model feedstreams using simple precipitating agents. This is a desirable separation mechanism as precipita-

tion reactions are energetically cheap at the expense of selectivity. Reaction-diffusion coupling can achieve the best of both worlds by imparting selectivity through many theoretical stages inside a column of gel. By using a gel loaded with precipitating agents, researchers at PNNL have separated elements in feedstocks representing NMC batteries,⁶⁶ neodymium magnets,⁶⁷ and even seawater.⁶⁸ Low-energy methods of separation, like those that use diffusion, evaporation,⁶⁹ and spontaneous reactions, are becoming increasingly more desirable as circularity of difficult-to-separate elements becomes a priority.

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Chapter 3

Methods

3.1 Small Angle X-ray Scattering

To look at a star by glances ... is to behold the star distinctly

Edgar Allan Poe

3.1.1 Theory

A brief introduction to small-angle X-ray scattering (SAXS) is required to understand the subsequent methods and SAXS data. When X-rays interact with matter, they either absorb or scatter. Absorption occurs at all wavelengths of light and coincides with the excitation of an electron to a higher energy state.¹ The exciton can rejoin the empty state it left through the generation of a phonon or photon, or it can be ejected entirely and leave behind an ion. For the purposes of understanding SAXS, the absorption and emission (fluorescence) of X-rays can be understood as contributing to the noise floor of measurement, as X-rays can be emitted chaotically towards the detector.^{1,2} This becomes a more important consideration for some elements on the periodic table and less for others.

Scattering can occur either coherently (elastic scattering) or incoherently (inelastic scattering). Coherent scattering is caused by the oscillation of electrons, which produce photons with the same energy and phase as the incident photon. Because the oscillating electrons are correlated with their neighbors, coherent scattering contains structural information that manifests as interference patterns at the detector. Incoherent

scattering contains none of this information since the photons lose energy after they collide, changing their wavelength.³ This contributes to the overall 'background' in the measurement, similar to fluorescence. Since the incident beam in a scattering instrument consists of a single wavelength, the structural information that is retained from the coherent scattering can be interpreted as regions of constructive or destructive interference depending on the phases of the scattered photons. On a 2D detector (Figure 3.1), this can manifest as peaks. As can be seen in Figure 3.1, the sample produces peaks that extend in a radial pattern across the 2D

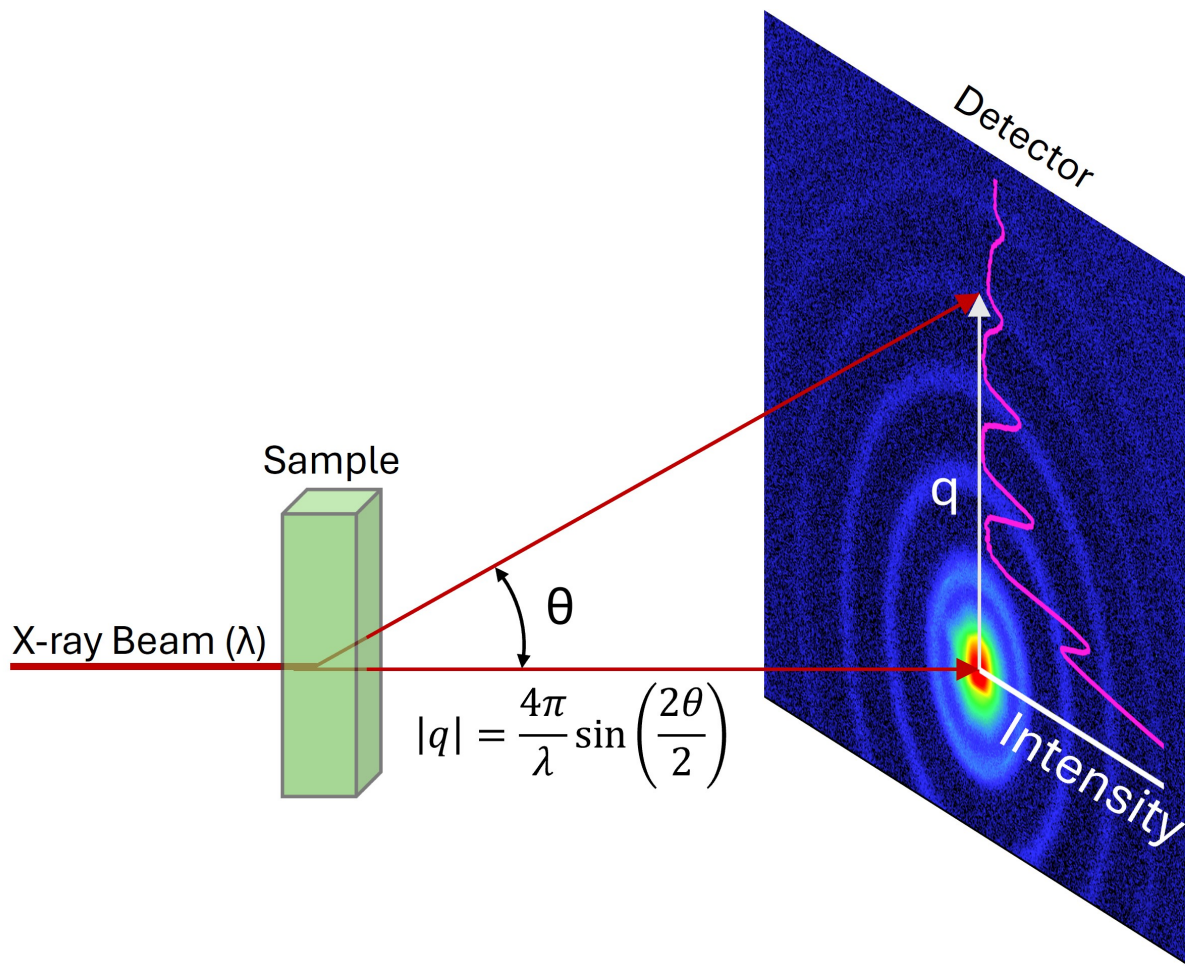


Figure 3.1: Small angle X-ray scattering diagram depicting a monochromatic X-ray beam traveling through a sample and coherently scattering at some angle θ . The X-rays are measured on a 2D detector as an intensity. A circular average of the 2D detector is taken to reduce the image to a 1D plot of the momentum imparted onto the scattered photons, q , versus intensity

detector. The distance from the center of the beam on the detector to where a scattered photon landed is the scattering vector, or momentum transferred to the photon, which is referred to as 'q' and has units of inverse

length. The angle θ in Figure 3.1 is equal to half the full scattering angle, and is often written as $\frac{2\theta}{2}$ because 2θ conventionally denotes the full deviation of the scattered beam from the incident beam. The convention follows from Bragg's law, in which θ is measured from the lattice plane rather than the beam axis and is therefore half the measured angle. The conversion from q-space (q) to real-space (d) from the definition of interference from a periodic spacing follows the same form as any conversion from reciprocal space to real space (Equation 3.1).

$$d = \frac{2\pi}{q} \quad (3.1)$$

Instruments are often referred to as having a 'q-range,' which is effectively the difference from the smallest to largest resolvable q value by the detector. Given that a detector can only be so large, and the beam necessarily obscures the smallest angles of scattered photons, the distance between the detector and sample can be altered to effectively change the q-range. As an example, the Xenocs Xeuss 3.0 instrument, which is the lab-scale instrument used in much of this thesis, adopts a moving detector. Depending on an instrument's configuration, the detector(s) may be fixed in place at specific angles or distances to achieve a similar effect.⁴ In some configurations, such as a Bonse-Hart configuration,⁵ single crystal silicon reflectors are used on either side of a sample to achieve ultrasmall scattering angles during 'rocking curve' measurements, which are more space efficient than having to move a detector further and further away to achieve a similar q-range. From Equation 3.1, it follows that features at smaller q values are the result of scattering from larger physical features. The absolute size ranges of features that can be distinguished depend heavily on the instrument and the scattering length density of the sample itself. Taking the 12-ID-E beamline at the Advanced Photon Source (Argonne National Lab) as an example,^{5,6} the range of sizes suitable for ultrasmall angle X-ray scattering measurements ranges anywhere from $30 \mu\text{m}$ to $1.5 \text{ \AA}^{-1}$ (Figure 3.2). This makes it possible to measure micrometer-sized particles and atomic lattices in the same experiment.

Both form and structural information are retained by coherently scattered photons. This makes it possible to create a mathematical model,^{7,8} or directly simulate,^{9,10} the scattering behavior of any arrangement of particles of any shape to fit a SAXS curve. The intensity of the scattered light with respect to q is proportional to both a structure and shape factor.¹¹ It is sometimes possible to quickly identify shapes by observing peak positions and slopes of two regions known as the Guinier region and Porod region (Figure 3.3). There is no specific value where these regions begin and end, as their position is size dependent, but they are

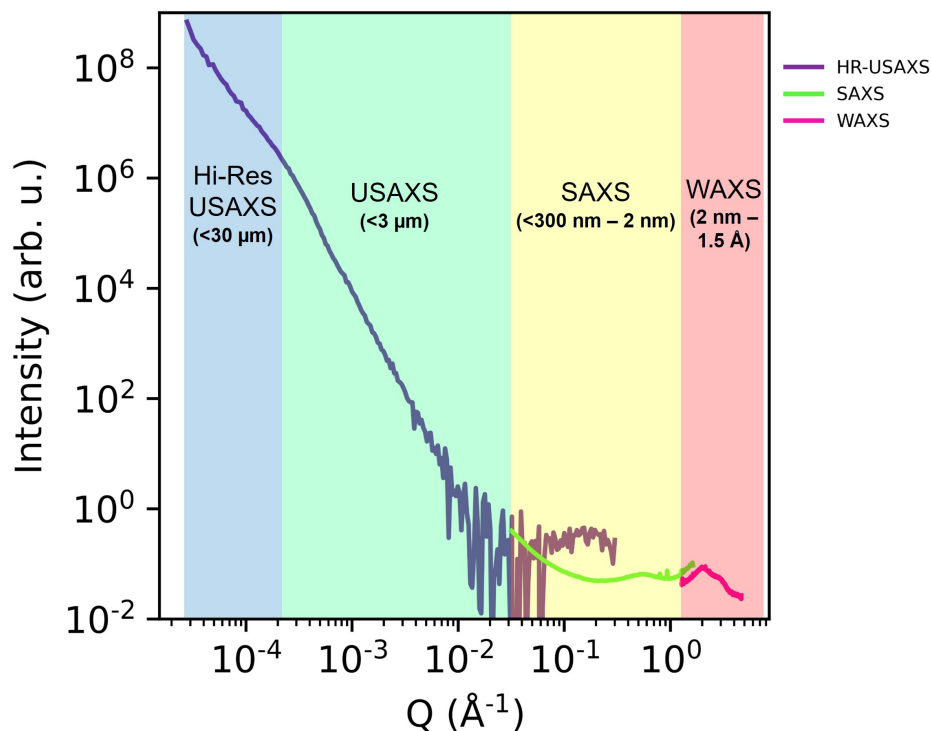


Figure 3.2: X-ray scattering data (HR-USAXS, SAXS, WAXS) taken at beamline 12-ID-E, Advanced Photon Source (APS), Argonne National Lab.⁶ Overlaid on plot is the approximate size ranges of the four techniques: high resolution ultrasmall-, ultrasmall-, small-, and wide-angle X-ray scattering (HR-USAXS, USAXS, SAXS, WAXS). HR-USAXS and USAXS at the APS utilize the same Bonse-Hart configuration with 440 and 220 Si crystals respectively, while SAXS and WAXS are measured from two detectors brought into position for sequential measurements.

useful descriptors nonetheless. The Guinier region has the lowest q values and is where information on the overall particle size can be found. The slope is also indicative of the shape itself. In spheres and cylinders, for instance, the slope is constant (q^0), while in lamellae its slope is q^{-2} .^{12,13} Depending on the feature, an inflection point or ‘knee’ where the slope changes can indicate the characteristic size of the particle. This can also represent the transition from the Guinier region to the Porod.

The Porod region lies at a q -range higher than the Guinier region, but before the transition to wide-angle X-ray scattering occurs. According to Porod’s law,¹⁴ the slope of this region follows a power law of q^{-4} . This arises from the Fresnel equations of reflection off a surface and requires a smooth, continuous surface. This makes fits of the Porod region useful for understanding the surface, or more broadly, the transition region between scatterers. A rough surface approximated as a fractal will have a power law slope between -4 and -3.¹⁵ It is common for solid surfaces like crystals to have a slope close to -4, while slopes between -2

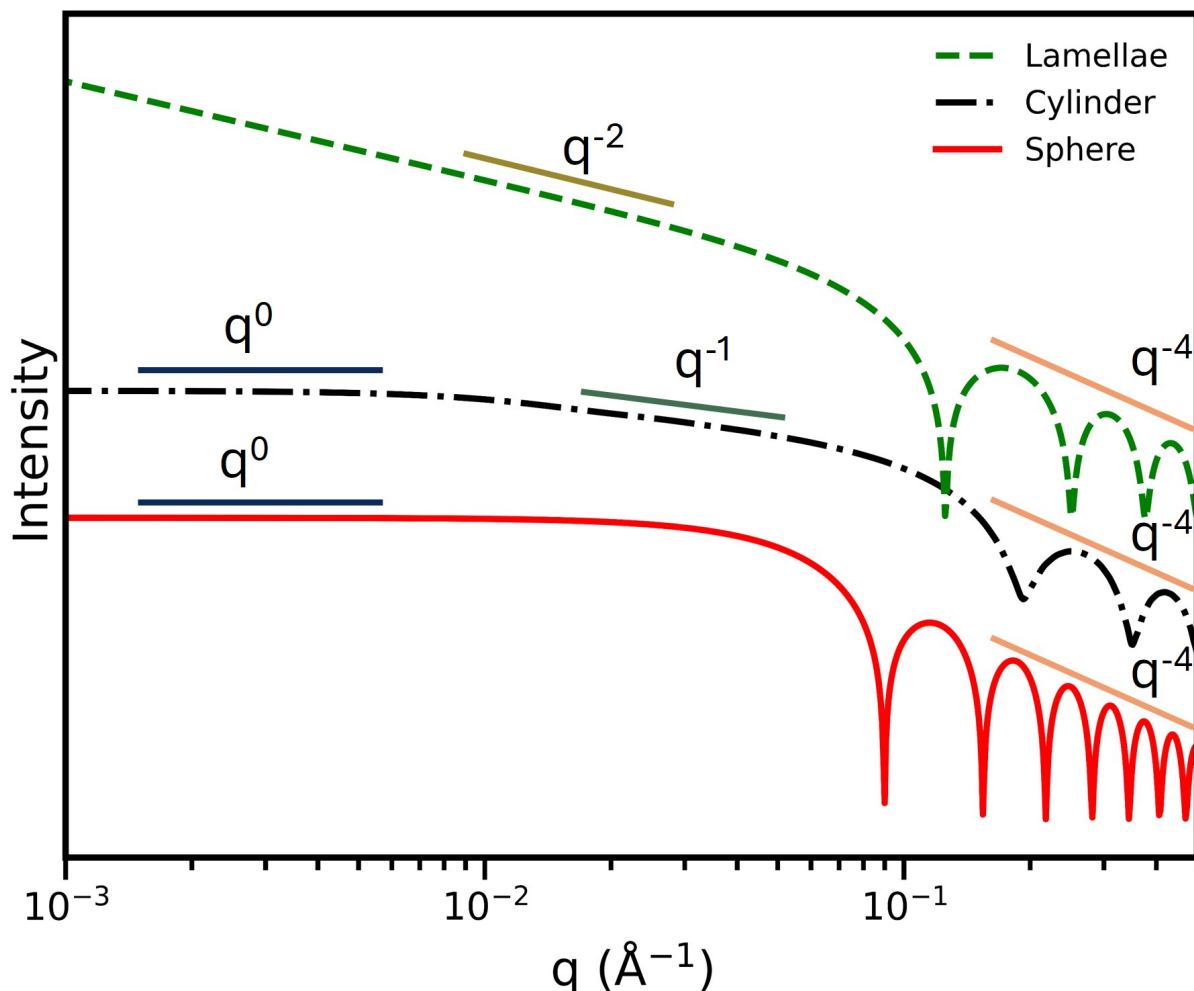


Figure 3.3: SAXS plot of scattering vector (q) against calculated intensity for a sphere (red, solid),¹² cylinder (blue, dash-dot),¹² and lamellae (green, dashed).¹³ The characteristic slopes at each region are identified.

and -3 will indicate a diffuse interface.

When the distances between particles become similar to their size, interference between them must be considered. The structure factor is similarly proportional to the intensity as a function of q and can result in peak formation in the scattering curve as the volume fraction of particles increases (Figure 3.4A). The curves in Figure 3.4A do not exhibit regular crystalline order, however. Assembled spheres with repeating subunits would exhibit Bragg peaks in the scattering curve identical to atomic unit cells in a crystal. In these cases, equation Figure 3.4 could be used to find the corresponding d-spacings of each peak in the lattice.¹⁶

Another significant attribute of a sample that can be represented in the scattering response is the polydis-

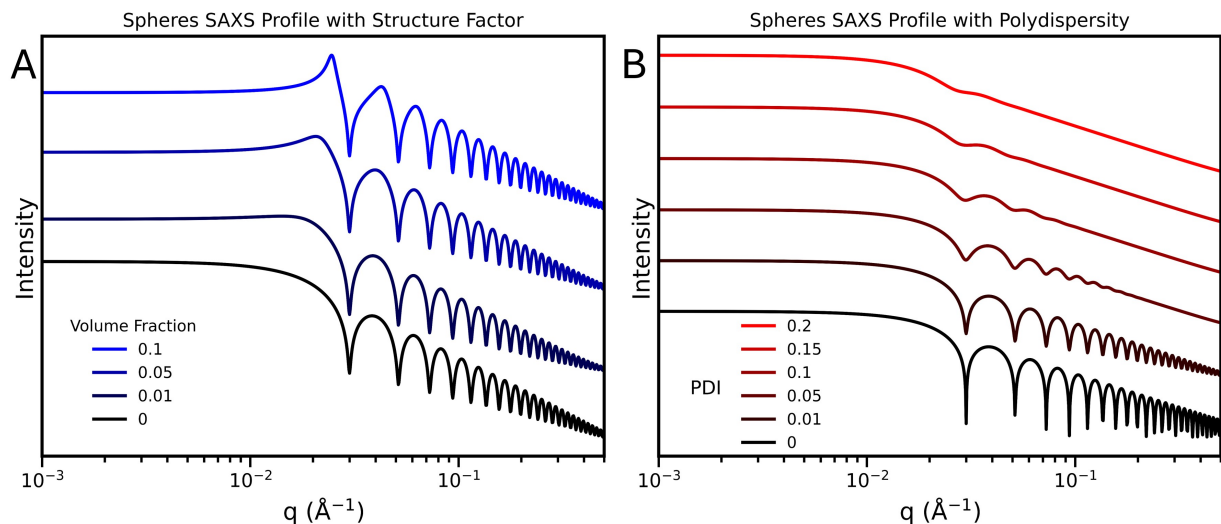


Figure 3.4: Calculated SAXS plots of 150 nm radius hard spheres with **A)** SAXS plot of the same spheres with a PDI of 0.01 and increasing volume fraction demonstrating the impact of the structure factor. The structure factor assumes hard spheres (Percus-Yevick).¹⁷ **B)** Increasing polydispersity index (PDI), which describes the distribution width (σ) by $\sigma = PDI \cdot r_{med}$, is the median radius.

persity of the features within the sample. Assuming a known shape, the size distribution can be determined from the scattering profile since the total scattering intensity is simply the sum of the contributions from all scatterers. The effect this has on the scattering is that the form factor peaks become smeared, as can be seen in Figure 3.4B. Polydispersity in scattering models is represented typically by a Gaussian distribution where a polydispersity index (PDI) is defined by a standard deviation, σ , and a mean feature size, x , by their ratio ($PDI = \sigma/x$). Practically speaking, for a simple sphere model, a PDI that is larger than 0.2 or 0.3 is close to the edge of the information limit of what can be meaningfully extracted from a sample containing spheres. This should be evident from Figure 3.4B as a PDI of 0.2 has almost entirely removed the oscillations from the scattering profile.

It is also possible to extract a more precise histogram of feature sizes by fitting the scattering profile with an arbitrary number of individual models. The result, if done properly in an ideal case, is a histogram of the sizes in the sample, which can capture more complicated multimodal distributions. This is the strategy some Monte-Carlo based methods adopt.¹⁸ Because the distribution is built up from many simple models rather than assuming a complicated size distribution beforehand, this approach can recover population shapes that would not be obvious *a priori*, and would be difficult to parameterize in a conventional fit. However, a

method like this suffers when applying more complex models with many parameters or conditions where there are many individual morphologies.

An additional theoretical consideration to make when approaching X-ray scattering is contrast. In scattering, a difference in contrast is required between the analyte and the matrix to obtain a meaningful measurement. In the same way that a white marker drawn onto a white sheet of paper is difficult to see, a scatterer surrounded by a matrix with a similar electron density would be nearly invisible. This is evident from the scattering equation (Equation 3.2) where the scattering intensity, $I(q)$, goes to 0 when the electron density of the particle, ρ_{particle} , and the matrix, ρ_{matrix} , are equal. In the full equation, N/V is the number density of the particle in the sample, V_{particle} is the volume of an individual particle, while $P(q)$ and $S(q)$ are the form and structure factors respectively. In many dilute cases, the structure factor, $S(q)$, which is related to the pairwise distribution of particles, is negligible and can be simplified to 1.

$$I(q) \propto \frac{d \sum(q)}{d\Omega} = \frac{N}{V} V_{\text{particle}}^2 (\rho_{\text{particle}} - \rho_{\text{matrix}})^2 P(q) S(q) \quad (3.2)$$

Just as $I(q)$ is low when contrast in electron density is small, the overall intensity of scattered X-rays also decreases as the number and volume of scatterers decrease. Importantly, the scattering scales with the square of the particle volume, V_{particle}^2 , while the dependence on the number density, $\frac{N}{V}$, is linear. Suppose we consider a solution with 1,000 spherical particles with a radius of 10 nm and a solution with a single particle with a radius of 100 nm. The volume of the larger particle is $4.188 \times 10^6 \text{ nm}^3$ while the smaller particle's volume is $4.188 \times 10^3 \text{ nm}^3$. Both samples would then have an identical $\frac{N}{V} V_{\text{particle}}^2$ prefactor since $1 \times 10^3 \cdot 4.188 \times 10^3 = 4.188 \times 10^6$. Therefore, to measure smaller particles, their concentration in solution has to be significantly higher than larger particles to achieve an equivalent signal. Another way to look at it is that scattering measurements are sensitive to small numbers of particles that would be difficult to find using traditional microscopy measurements. After all, a single 100 nm particle scatters with the same intensity as a thousand 10 nm particles in our example. This is not to say, however, that the two populations of particles in the same sample would be indistinguishable. Their different sizes would produce scattering features at different q values regardless of concentration.

From Equation 3.2, it is also important to notice that in the case where all scatterers are identical, the scattering scales with the square of the difference in electron density. The consequence of this is that

identical scattering behavior can be produced if the electron densities of the scatterer and the medium were reversed. For this reason, it is impossible to determine from scattering alone which parts of a sample are electronically dense. This is referred to broadly as the Babinet principle, and often, especially in soft matter applications, it is important for the experimenter to carefully define what the analyte actually is. To illustrate this, Figure 3.5 demonstrates the case of an image of a single particle in a square, empty field. A binary mask of the particle is made (Figure 3.5A), where the particle area is given a value of 0 (black) and the surrounding field is given a value of 1 (white). Then, the values are inverted, where the particle becomes 1 and the field is 0. From the masks, a fast Fourier transform (FFT) is performed (Figure 3.5B), which is the same mathematical transform as scattering behavior due to the Born approximation.¹⁹ A radial average is then taken of the FFTs, and both are plotted over a log-log axis with arbitrary units (Figure 3.5C) along with the analytical scattering model for a sphere. The residuals are also plotted below as the ratio of the 'scattering' intensity for the image and its inverse.

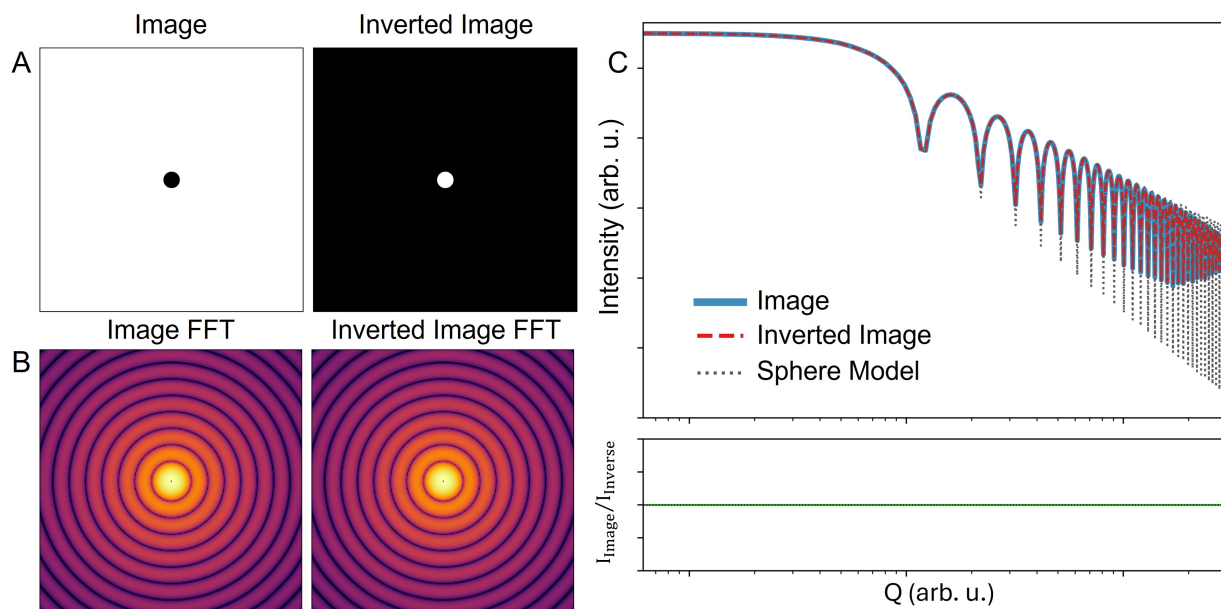


Figure 3.5: Example of the Babinet Principle on the simple example of a single spherical particle. **A)** 2D image masks of a black particle on a white field and a white particle on a black field. The real world mirror being a spherical particle in a solution with a lower scattering length density and a spherical hole in a solid with a high scattering length density. **B)** Fast Fourier transforms (FFTs) of the two images and **C)** radial profile plots of the two FFTs which display an identical 'scattering' profile. The two plots are identical as can be seen from the ratio of the radial profiles.

From the radial profile plots, the shape of the two objects is easily identified as spherical given the flat

slope after the knee in the Guinier region and its alignment with the model. However, from an experimenter's perspective, the black particle might be considered a spherical precipitated crystal of a certain radius, while the white particle could be described as a small pore in the cross-section of a material. Yet the two structures with the same form factor, structure factor, concentration, and size are indistinguishable from one another in scattering. This makes it especially important for the experimenter to define their model appropriately and corroborate the scattering measurements with additional analyses. This is especially important to understand when analyzing gels with scattering, as voids filled with water and dense regions of polymer can appear similar in the scattering profile.

3.1.2 Practice

Sample Preparation

The ease and flexibility of SAXS sample preparation is what makes the technique so applicable to such a wide range of applications. The only real constraints on sample preparation are that the sample be thin enough that the X-ray beam can transmit sufficiently but not so thin that scattering is negligible. The other consideration to make is that in most cases, lab-scale instruments will utilize an evacuated chamber to measure scattering to limit the parasitic scattering from air. This means airtight sample holders are often required. For liquid samples, quartz glass capillaries are often loaded and then sealed with an epoxy or hard wax. Vacuum-sensitive pastes or gels are usually loaded into cartridges either bolted together with an O-ring or rubber spacer with windows made from a transparent film like Kapton. Dry solid samples like powders that don't require sealing can be held in place with transparent tapes or films like Scotch or kapton tape. Some solid samples that are thin enough to transmit do not need any support at all, making a container unnecessary, and simply taping them directly to a sample holder is acceptable. Just like with any analysis, a scattering measurement is improved by reducing the signal from the background, so thin-walled sample containers will always improve the results of the measurement.

For some experiments, the thickness of the sample is flexible. The question then becomes, how thick exactly should the sample be? It is naive to assume that the thinnest sample, which gives the best transmission, will produce the best data. An incredibly thin sample that lacks scatterers would just result in poor signal-to-noise after subtraction of the background. A different problem presents itself if the sample is

too thick. Too many scatterers can result in excessive secondary scattering where photons scatter multiple times before exiting the sample, destroying the structural information. In many cases, a sample that scatters poorly can be overcome by increasing the measurement time, which improves the sampling statistics. Since the sampling is a random distribution of detector counts, the standard deviation of the integrated intensity is proportional to the square-root of the total number of counts. To reduce the noise by a factor of two then, it is necessary to measure four times longer.²⁰ This is, of course, a trade-off as many samples are dynamic on longer time scales, and in many instances, a large number of samples are being run simultaneously. Ultimately, an instrument capable of a higher flux is preferred when fast measurements are desired.

Lab Scale and Synchrotrons

Synchrotrons offer a high flux for cases such as these, where flexibility in the sample thickness and fast measurements are required. Unlike a lab-scale instrument, however, which typically has much more availability than a synchrotron, determining the correct sample thickness by directly measuring on the instrument itself is not possible. It must be calculated beforehand instead. The intensity of the scattered photons can be calculated using the sample's attenuation coefficient and the wavelength of the radiation to plot the intensity against the sample thickness. This was done for pure water in Figure 3.6. In Figure 3.6A the transmission of scattered light at the $k\alpha$ of copper (1.54 Å, 8.05 keV) was calculated using the Beer-Lambert attenuation equation, Equation 3.3, where μ is the attenuation of the sample at the incident wavelength and t is the thickness of the sample. The ratio of the transmitted light, I_{trans} , to the intensity of the incident light, I_0 , is the normalized transmitted light with respect to material thickness, $T(t)$.

$$T(t) = \frac{I_{\text{trans}}}{I_0} = e^{-\mu t} \quad (3.3)$$

The number of scatterers in the sample, $S(t)$, grows linearly with thickness and the scattering attenuation coefficient, μ_s .

$$S(t) \propto \mu_s t \quad (3.4)$$

The intensity of scattered light that reaches the detector is calculated by integrating over the entire thickness of the sample where a photon enters, is attenuated over some depth z , scatters at some slab dz , and finally

is attenuated on the way out of the sample over $t - z$ before exiting the sample.

$$I_s(t) = I_0 \int_0^t e^{-\mu z} \mu_s e^{-\mu(t-z)} dz = I_0 \mu_s t e^{-\mu t} \quad (3.5)$$

The measured intensity of scattered photons increases with thickness up to a point before it decreases as the sample becomes too thick to transmit any light at all. The thickness where scattering intensity is at its peak is when $dI_s/dt = 0$. Therefore,

$$\frac{d}{dt} (t e^{-\mu t}) = e^{-\mu t} (t - \mu t) = 0 \Rightarrow t_{\text{opt}} = 1/\mu \quad (3.6)$$

The optimal thickness for the sample, t_{opt} , where the scattered intensity is highest is then simply the inverse of the sample's total attenuation coefficient, μ , at the wavelength of the incident beam.

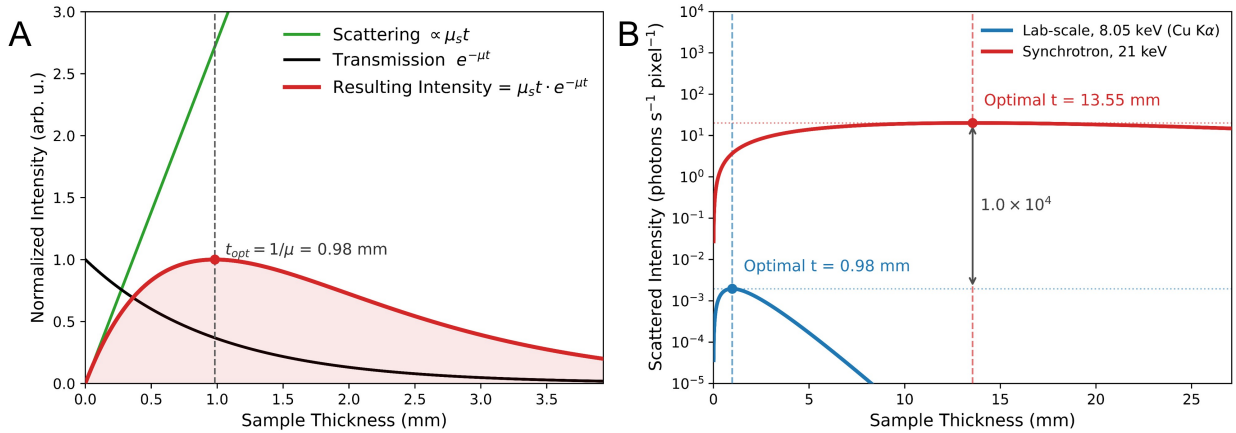


Figure 3.6: **A)** Water's transmission (black), scattering (green), and the resulting intensity (red) of X-rays at the Cu $K\alpha$ edge (1.54 Å, 8.05 keV) as a function of sample thickness. **B)** The resulting scattering intensity representing the flux and wavelength of a lab-scale instrument (8.05 keV, 4.5×10^8 photons/s) and a beamline at a synchrotron (21 keV, 1×10^{12} photons/s). The lab-scale and synchrotron comparison assumes the same detector distance and type of Si detector, which would have a $\sim 0.33\%$ efficiency above 20 keV compared to $> 99\%$ at the Cu $K\alpha$ edge.²¹ Attenuation coefficients for water were obtained from NIST.²²

To illustrate the difference in capabilities between a synchrotron light source and a lab-scale instrument, in Figure 3.6B the total scattering intensity of a water sample with respect to thickness is plotted for a lab-scale instrument that has a flux of 4.5×10^8 photons/s at a wavelength of 1.54 Å (8.05 keV) and a beamline at APS (beamline 12-ID-E, USAXS/SAXS/WAXS).⁵ This beamline has a typical flux of 1×10^{12} photons/s

at a wavelength of 0.602 Å (21 keV). This energy makes it possible to penetrate thicker samples, while the flux enables even more photons to reach the detector, improving counting statistics for measurements. The result is that the thickness of a water sample in the lab-scale instrument has an optimal thickness of 0.98 mm, which quickly drops off, while the synchrotron can measure water samples many tens of millimeters larger with an optimal thickness of 13.5 mm. In fact, the synchrotron at 21 keV can theoretically transmit through up to 250 mm of water. Another consequence of the enhanced flux at a synchrotron is the ability to filter out more incoherent X-rays to produce a more coherent beam. This results in higher resolution, less smearing, and allows incredibly small micro- or even nano-sized beams to be used.

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3.2 Electron Microscopy

A measurement is oftentimes limited by the effective size of its 'yardstick,' or, the smallest resolvable dimension of the probe. For optical imaging techniques, the 'yardstick' can be thought of as the wavelength of light interacting with the subject. The smaller the subject is, the smaller the wavelength of light needs to be to have a high enough resolution to discern its features. The optical limit, or diffraction barrier, is approximately half of the wavelength of light, which gives optical microscopes an approximate resolution of around 200 nm with light in the visible spectrum (400 - 700 nm). To achieve a reasonable amount of detail, a shorter yardstick is needed, and we need not be limited to photons. Electrons have a wavelength in the picometer range (0.002 to 0.005 nm), giving them a theoretical resolution limit of less than 0.01 nm. Electron microscopes make use of the transmission or scattering of electrons to measure features well beyond what an optical microscope is capable of, unlocking the nanoscopic world. Electron microscopy is a workhorse of materials characterization, but there is, of course, no single electron microscope for all imaging tasks. This section will discuss two broad categories, scanning electron microscopes (SEMs) and transmission electron microscopes (TEMs). Both rely on fundamentally the same physics, but their differences in power and construction make them better suited for different but related tasks. This methods chapter will discuss the practical theory and relevant sample preparation considerations relevant to this thesis. For a more in-depth discussion on SEM, Ul-Hamid (2018) is a good resource,¹ while for TEM, Williams and Barry (2009) is the most common reference for beginners despite its age.²

3.2.1 Scanning Electron Microscopy

Theory

Scanning electron microscopy (SEM) utilizes the short wavelength of electrons to resolve nanoscale features in samples over an incredibly wide size range. Magnifications of 1,000,000x are common, and a larger depth of field than optical microscopy makes rough surfaces stay in focus. A high energy (0.5 to 30 kV) electron beam is directed towards a conductive sample where the emerging electrons, photons, and X-rays are used to form the image. The beam interacts with the sample to produce a teardrop-shaped interaction volume whose size is dependent on the energy of the electron beam and the atomic number of the elements in the sample. Figure 3.7 illustrates the interaction of the beam with matter that results in scattering and emission. In SEM, the electrons that are scattered back towards the detector and the electrons that are emitted, either through secondary emission or an Auger emission, make up the image. Electrons that penetrate the sample are either transmitted or scatter deeper into the sample and are not detected. Backscattered electrons maintain most of their energy, while secondary electrons and Auger electrons that are emitted are much lower in energy. Backscattered electrons, therefore, can be detected from deep within the sample, while emitted secondary and Auger electrons are only detectable if they are produced at the material surface (<10 nm).³ This makes them incredibly sensitive to surfaces and edges, and detectors that measure them give better definition at the edges of samples.⁴

By targeting the energy of the electrons and selectively filtering backscattered or secondary electrons, topographical mapping is possible. The production of a secondary electron is also accompanied by characteristic X-rays with energies that match the energy of the secondary electron's state. This produces a characteristic spectra that can be used for elemental analysis in what is known as energy dispersive spectroscopy (EDS). The electrons that are produced by the relaxation of an excited atom are Auger electrons. These also have a characteristic energy and can be used for elemental analysis by a scanning Auger microprobe (SAM) or Auger electron spectroscopy (AES). This is a less common technique than EDS however, and the main difference between the two is sampling depth. EDS samples between 1 and 3 microns of a sample while AES is purely a surface technique (<10 nm) as the electrons have too low of an energy to escape from deep within the sample.⁵

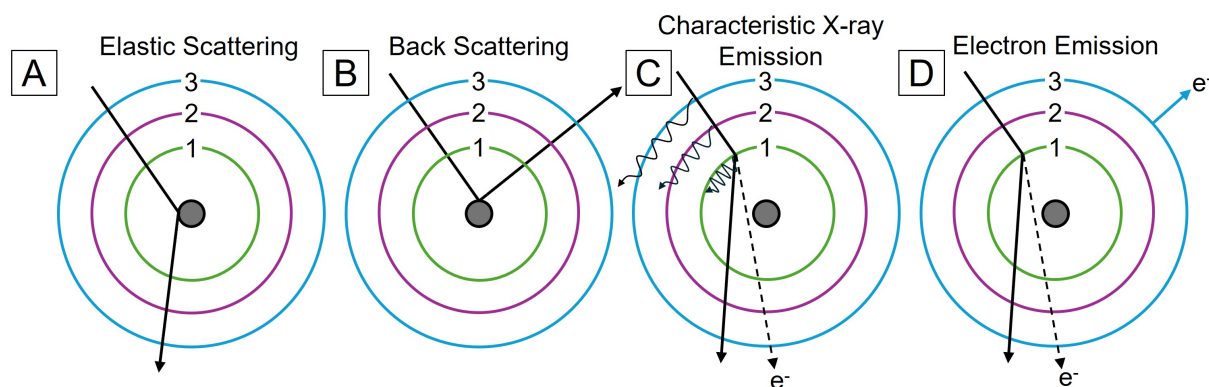


Figure 3.7: Graphic of accelerated electron's interaction with matter. Depicted is **A)** elastic scattering, **B)** backscattering, **C)** the emission of characteristic X-rays, accompanied by a secondary electron (dotted arrow), and **D)** the emission of an Auger electron (blue arrow) and secondary electron (dotted arrow). Reproduced from Ali *et al.*,³ licensed under CC BY 4.0.

Practice

Energy dispersive spectroscopy is an incredibly powerful tool for determining the elemental composition of a material. The energy of the X-ray emitted from a sample bombarded by the electron beam has energies specific to the electron orbitals they emitted from. The X-rays are recorded by the detector and plotted in a histogram as total counts or counts per second on the y-axis and energy on the x-axis. The number of counts is related to the concentration of the element in the sample, and higher concentrations of an element will produce higher counts. This technique is best suited to the detection of heavy elements, as the more tightly bound core-shell electrons emit higher energy photons that are less likely to be blocked by the sample itself, as well as the window covering the detector. Because of this, EDS detectors are unable to measure the lightest elements, hydrogen, helium, and lithium, since X-rays of those energies are blocked by the Formvar window over most EDS detectors.¹ There is an additional limitation in the accuracy of the quantitative measurement of element concentration given the fundamental distribution of energies for the characteristic X-rays. The full-width-half-max of the peaks tends to be around 150 eV wide,⁶ which causes overlap between elements with similar energies. This is typically a non-issue, but for measuring similar elements like cobalt, nickel, iron, and manganese or chromium, vanadium, and titanium, which have overlapping $K\alpha$ and $K\beta$ lines, it can cause inaccuracies. Especially when the total concentration of the elements is low.^{7,8} The accuracy of EDS at the best of conditions is 0.2 wt%, which also requires that you roughly

know the elemental makeup of your subject to properly fit the spectrum. WDS (wavelength dispersive spectroscopy), however, uses a diffracting crystal to filter unique wavelengths and boasts accuracies as high as 0.001 wt%.¹ This is why EDS is best suited as a semi-quantitative technique for creating maps of element locations, which can be paired with an elemental characterization technique like ICP-MS to determine more precise compositions. Additionally, EDS suffers in accuracy, like any imaging technique would, when the topography of the sample prevents characteristic X-rays from reaching the detector. This manifests as a slower count per second. The elemental maps are created as the probe scans over the sample and produces a spectrum at each discrete position. The resolution of the map is typically much less than the image produced from the backscattered and secondary electrons, so characterizing individual smaller particles can be a challenge.

In practice, sample preparation for electron microscopy is easier than most. The most important consideration to make when preparing an SEM sample is its conductivity. A non-conductive sample will accumulate charge when bombarded with an electron beam, which creates artifacts in the image if the electric charge is not dissipated through the conductive sample holder. This could appear as beam drift, bright spots, or blurry regions. Conductive carbon tape is often used to affix samples to a metal sample holder, and for biological samples, a sputtered gold coating can be used to improve conduction. Samples with retained moisture similarly accumulate charge, which is why most SEM samples (except those in extremely low vacuums and probe voltages) have to be entirely dried.

3.2.2 Transmission Electron Microscopy

Theory

Transmission electron microscopy (TEM) is a powerful technique for imaging extremely small subjects, even as small as lattices of atoms. In contrast to SEM, which primarily images using backscattered and emitted electrons, TEM uses a high-energy beam (80-300 keV) to transmit entirely through a sample. Since the underlying physics of electron scattering is the same, the contrast in the image arises from how the electrons are scattered by the specimen. Since the detectors are placed behind or below the sample (Figure 3.8), the position of the detector greatly affects the scattering selection. Bright field (BF-TEM) is the most commonly used, where the detector is positioned in line with the beam. This detector receives only

the unscattered electrons, which makes the strongly scattering regions appear darker, either because they are thicker or are made up of heavier elements. Unlike in SEM, TEM can often forgo a rastering electron beam in favor of flooding a broad stationary beam over a sample. This makes the formation of an image simple, as the image cast on the 2D detector is a direct projection of the subject. In fact, a phosphor plate that illuminates when bombarded with electrons is often used to view the produced image with the stationary beam.

Dark field (DF) and high-angle annular dark field (HAADF) are both similar in that they selectively measure the more strongly scattered electrons. This produces a contrast-inverting effect in images where the highly scattering regions appear extremely bright compared to their surroundings. DF and HAADF can also improve contrast in imaging as weakly scattering regions can be identified more easily compared to the substrate. The detectors are typically placed annularly around the central BF detector as seen in Figure 3.8. While the stationary beam is the most typical mode for older instruments, the newest generation of TEMs can almost always function as both a scanning transmission electron microscope (STEM) and a conventional transmission electron microscope (CTEM). The scanning capability makes it possible for STEMs to perform EDS in the same way a SEM would function (Figure 3.8). STEMs typically have improved resolution for EDS imaging compared to an SEM due to the higher energy and lens architecture, but they still suffer from a reduced resolution when creating elemental maps compared to typical operation.

Practice

The most immediately apparent difference between SEM and TEM to a researcher is the sample preparation. While SEM is a surface characterization technique, TEM characterizes the internal structure of a sample and requires complete transmission. The subject, as well as the substrate, needs to be thin enough for transmission. While it may be possible to investigate the edges of micrometer-sized particles using TEM, nanoparticles or thin films are typically better suited and require much less preparation. Williams and Barry have an extensive discussion on preparing bulk samples for TEM.² The substrates that support TEM samples are typically copper or nickel mesh, which can be purchased with or without a carbon or Formvar coating layer. A diagram of this can be seen in Figure 3.9. The choice of TEM grid depends greatly on the subject one would like to image. In samples with a higher contrast (strongly scattering), such as gold nanoparticles,

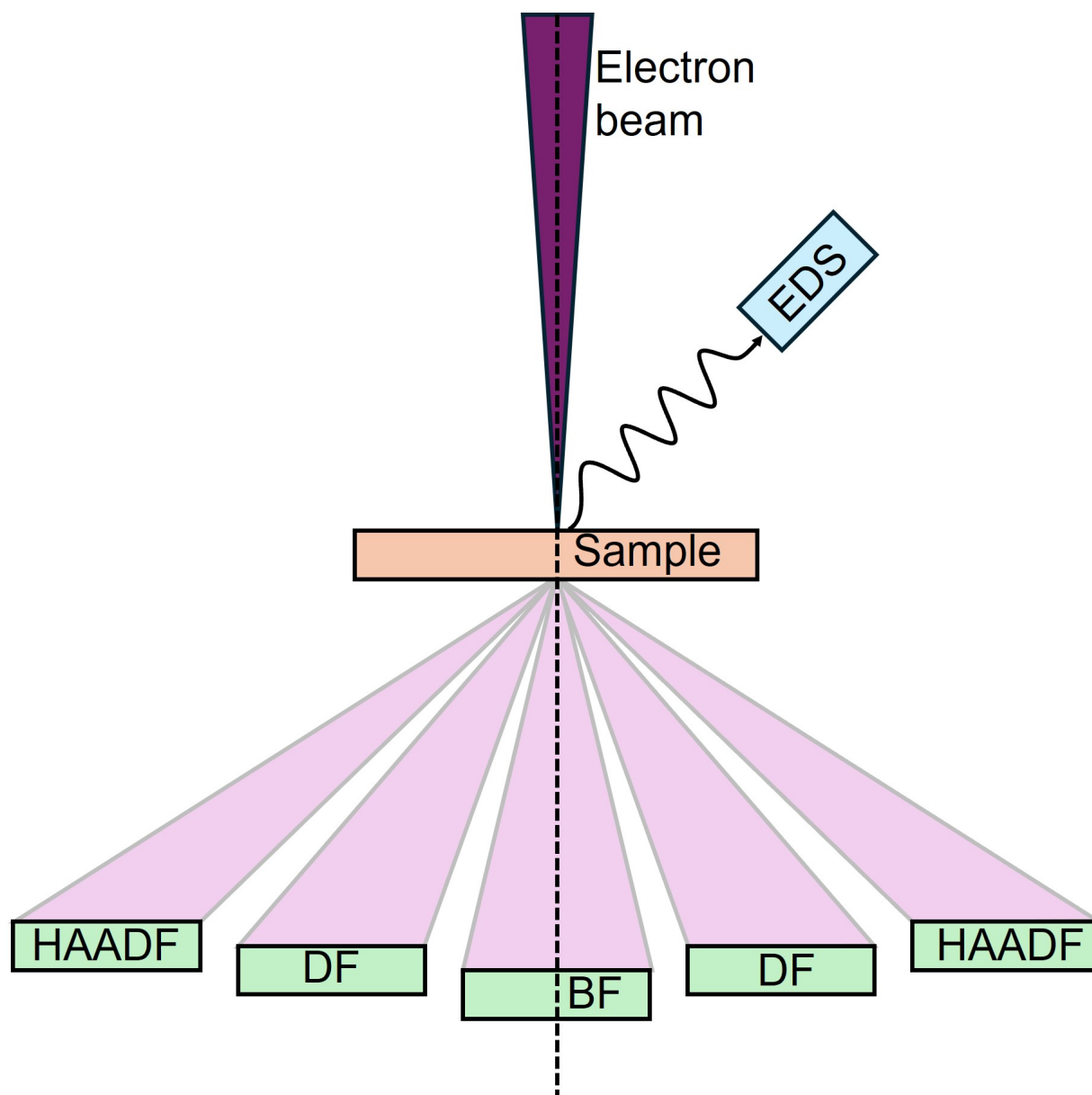


Figure 3.8: Graphic of electron detector positions in a TEM for high-angle annular dark field (HAADF), dark field (DF), bright field (BF), and energy dispersive X-ray spectroscopy (EDS).

a copper mesh with a carbon layer is likely all that is needed. For small particles of lighter elements where contrast is low, eliminating the scattering from the background with a single-layer graphene film on a carbon mesh might be required. Formvar is an alternative option that provides a much smoother and more durable support surface. Between these Formvar and carbon grids, there are a plethora of choices to make regarding thickness and structure. It is possible to find smooth films of both at every thickness imaginable, as well as

films that are covered in large gaps called lacey or holey carbon or Formvar.⁹ The holey and lacey varieties simply provide larger samples with opportunities to overhang or span the gaps in the substrate so that an image can be made where there is no substrate beneath the subject. To image the assembly of particles, however, lacey or holey grids provide a very uneven surface that doesn't allow for long-range ordering to present itself.

TEM Grid Construction

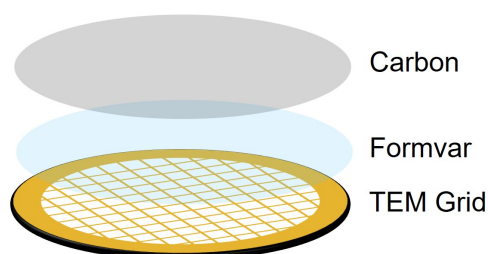


Figure 3.9: TEM grid construction. Shown is a copper mesh with a layer of Formvar and carbon thin film. TEM grids can be found with Formvar only, carbon only, both Formvar and carbon, or neither.

While there are innumerable ways to prepare any material into a TEM sample and place it onto a grid, this section will focus entirely on nanoparticle samples. These are probably the simplest materials to prepare for a sample, as the prep predominantly involves the suspension of the particles into a volatile solvent and dripping them onto a TEM grid where they are allowed to dry (Figure 3.10A). The methods for preparation involve tuning the volatility of the solvent and the method of introduction to control the number of particles and the rate they are deposited onto the substrate. In many cases, where the information of interest is particle morphology or crystal structure, it is enough to simply place 2-3 drops of a very dilute solution of nanocrystal onto the TEM grid and allow it to fully dry. While 'very dilute' is not the most quantitative description, it really depends on the nature of the particles and the solvent to determine the concentration required. For a heuristic, 10 μL of the concentrated nanoparticle stock solution per milliliter of the solvent is a good starting point for the dilution.

When assembly of the nanoparticles is of interest, however, the methods can become slightly more involved. Dip coating, where the grid is held in micro tweezers and slowly lowered either entirely or partially into a solution of colloidally stable nanoparticles, can produce some of the cleanest results with large areas

of tightly arranged particles (Figure 3.10C).¹⁰ This takes advantage of the surface tension of the solution wicking up the sides of the grid, depositing particles through the evaporative convection. Another popular technique to induce assembly is to place a droplet of a very dilute and purified colloidal nanoparticle solution carefully onto a grid suspended in tweezers, rather than lying directly on filter paper, and allowing the droplet to slowly dry (Figure 3.10B).

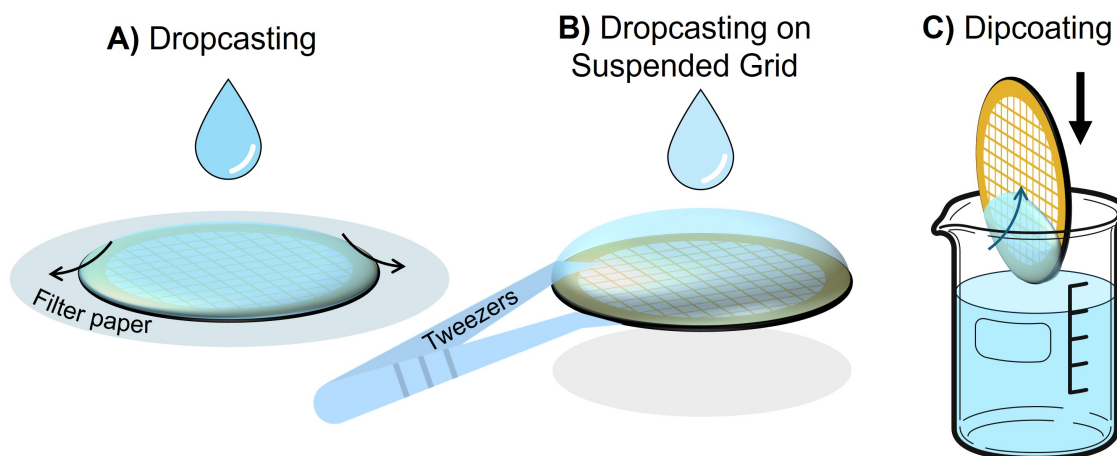


Figure 3.10: TEM sample preparation methods for subjects suspended in a volatile solvent (water, ethanol, chloroform, etc). **A)** A fast-drying dropcasting method with a TEM grid placed onto filter paper using a dilute sample solution. **B)** A slower drying method with a very dilute solution placed gently onto a suspended grid to allow slow settling of particles. **C)** A fast-drying dipcoating method where a TEM grid is partially dipped into the sample solution to pull the sample onto the grid with wicking and convective evaporation.

It is here where a warning should be made. Imaging of any kind is biased to the field of view projected onto the detector. It is dangerous to draw anything more than qualitative conclusions of things like particle size, monodispersity, and assembly behavior from a TEM image. It is exceedingly common for the TEM sample prep to select for particles of a certain size, introduce assemblies that don't represent typical behavior, and poorly measure size distributions given a single statistically irrelevant population. Because of this, TEM images are at best representations and, at worst, fictions of the subject. This is especially relevant to the field of synthesis, as it is commonplace for misrepresentations of syntheses to be made by naturally being selective in the reported images. It is also important to report, in as much detail as possible, the method of sample prep and to scrutinize any images submitted without this description. This is why, whenever possible,

imaging should be paired with statistically relevant bulk sampling characterization techniques. It is for this reason that scattering techniques and electron microscopy are such a powerful approach for characterizing morphology. Microscopy can indicate in broad strokes what is inside the sample, which then informs the models used to fit the scattering data. While scattering can describe size, shape, and structure rapidly and *in situ* with statistical relevancy.

3.2.3 References

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Chapter 4

Synthesis, Assembly, and Electrochemical Performance of Ultrasmall Sb₂S₃ Nanoparticles

4.1 Chapter Introduction

This chapter concerns work that was published in the Royal Society of Chemistry's Journal of Materials Chemistry A titled "Synthesis, Assembly, and Electrochemical Performance of Ultrasmall Sb₂S₃ Nanoparticles".¹

Antimony(III) sulfide (Sb₂S₃) is an environmentally friendly material of interest for thermoelectric,^{2,3} photovoltaic,⁴⁻⁶ and electrochemical applications.⁷⁻⁹ It is found naturally in a layered orthorhombic phase (*Pmna*), where it has been known since antiquity as stibnite,¹⁰ but under certain conditions an amorphous phase is also accessible.^{11,12} As is the case with many metal chalcogenide systems, Sb₂S₃ benefits from nanostructuring, particularly in colloidal synthesis routes, to improve and tailor its properties.^{9,13} Colloidal nanoparticles have larger specific surface areas, tunable sizes, morphology dependent properties, and are solution processable.¹⁴ Because of this, expanding the library of colloidal synthesis routes towards useful morphologies of Sb₂S₃ has continued to be impactful to a diverse range of technologies.¹⁵⁻¹⁸ Sb₂S₃ has been synthesized colloidally using a variety of methods producing several structures and forms. Since

the most thermodynamically stable product is crystalline orthorhombic, micro and nanoparticles commonly manifest as wires,¹⁹ bundled rods,²⁰ and even ‘flowers’.²¹ In contrast, the amorphous phase is spherical when synthesized using solvothermal bottom-up strategies.^{9,15,22,23} Sizes for particles, crystalline and amorphous, range from ~ 20 nm to many hundreds of micrometers, but some cases of smaller nanoparticles (< 10 nm) also exist in literature.^{17,24}

The synthesis of ultrasmall colloidal particles, defined as particles smaller than ~ 5 nm in diameter, can often require highly involved procedures.²⁵ At these sizes, unstable atomic arrangements become easier to access due to the increase in surface area relative to volume.²⁶ Magic-sized clusters, having specific numbers of atoms producing stable structures, are a prototypical example exhibiting unique optical characteristics and self-assembly.²⁷ Nanoparticle assembly into stable structures is affected by the shape and morphology of the particles,²⁸ by the use of templates (e.g. patterned surfaces or self-assembling polymers),^{29,30} by surface bound ligands,³¹ by external fields,³² and by registered crystallographic directions. With respect to crystallographic registry, this can be mediated either through the attachment of specific facets,³³ or by the facet-specific capping of ligands which can influence alignment of nanocrystals during packing.³⁴ Because of this, the nanoparticle structure and morphology are strong predictors for highly ordered self-assembly in the absence of a template or external field. For example, large aspect ratio nanostructures pack into hexagonal arrays,^{35,36} and monodisperse spheres typically experience close packing into face-centered cubic or hexagonal close-packed lattices.^{37,38}

Sb_2S_3 has also received significant attention as a battery material for both Li^+ and Na^+ ion systems. It is able to undergo both alloying and conversion reactions with Li^+/Na^+ at the negative electrode giving it a theoretical capacity of 946 mAh g^{-1} compared to graphite’s 372 mAh g^{-1} .⁷ Its rate capabilities are also impressive, with certain Sb_2S_3 electrodes able to withstand cycling at rates up to 20C (~ 3 min charge/discharge).⁹ As such, Sb_2S_3 stands to be impactful in electrifying machines that draw large currents or benefit from faster charging than what current battery technologies can support.⁷ One challenge with Sb_2S_3 is that the highest performing batteries are exclusively made using bottom-up processes to produce a nanoscale active material,^{9,39,40} which complicates production at relevant scales and low cost. The commercialization of Sb_2S_3 as an electrode material would greatly benefit from simplified synthetic procedures that lower the cost of preparation.

To this end, we synthesize ultrasmall antimony(III) sulfide (Sb_2S_3) nanoparticles (<4 nm) using a simple one-step, room temperature, procedure in open air. Small angle x-ray scattering (SAXS) measurements demonstrate that these nanoparticles assemble into unusual long-range hexagonal ‘rod-like’ packings, which we attribute to a non-uniform coating over the surface of the particles. The spacing and structure of the arrangement can be fine-tuned by changing the composition and length of the alkylamine ligands and solvent. The Sb_2S_3 nanoparticles also exhibit impressive electrochemical performance when prepared as a negative Li^+ and Na^+ ion battery electrodes. Different ligands influence the packing arrangement, and electrochemical data shows significant differences between these samples even after a ligand exchange. Thus, the identity of the ligand used in the synthesis of Sb_2S_3 nanoparticles has significant impacts for assembly as well as electrochemical performance.

4.2 Experimental

4.2.1 Materials

All chemicals were used as received unless specified otherwise. Antimony(III) acetate ($\text{Sb}(\text{OAc})_3$, 99.99% trace metals basis), ammonium sulfide solution ($(\text{NH}_4)_2\text{S}$, 20wt% in water), ammonium sulfide solution ($(\text{NH}_4)_2\text{S}$, 40–48 wt% in water), octylamine (OcAm, 99%), dodecylamine (DoAm, 98%), oleylamine (OAm, $>98\%$ (primary amine)), trioctylphosphine (TOP, 97%), trioctylphosphine oxide (TOPO, 99% Reagent-Plus), hydrazine monohydrate (N_2H_4 , 64–65%), were purchased from Sigma-Aldrich. Toluene, ethanol, and other common solvents were purchased from Fischer Scientific and used as received.

Battery grade 1.0 M LiPF_6 in EC/DMC = 50/50 (v/v), propylene carbonate (99.7%), sodium metal ($>99.99\%$, dry cubes, ACS Specification), sodium carboxymethyl cellulose (CMC) ($M_w \sim 90,000$) were purchased from Sigma Aldrich. Sodium perchlorate ($\geq 98\%$) was purchased from Fisher Scientific. Fluoroethylene carbonate ($\geq 98\%$) was purchased from TCI America. Carbon black (Vulcan XC72R) was purchased from Cabot Corporation and stored in a vacuum oven at 80°C . CR2032 Coin Cell Cases (SS316 Option), CR20XX Stainless Steel Spacer (15.5 mm Dia $\times$ 0.4 mm), Stainless Steel Wave Spring, Copper foil ($>99.99\%$, 9- μm thickness), 600 μm thick Lithium chip (Battery R&D grade) were purchased from MTI Corporation. Celgard separator (Celgard 2400, 25 μm microporous monolayer polypropylene membrane,

Celgard Inc. USA), glass microfiber separator (GF/D, Cat No. 1823–257, Whatman).

4.2.2 Synthesis of Ultrasmall Antimony(III) Sulfide Nanoparticles

The synthesis of ultrasmall Sb_2S_3 was adapted from a procedure used by Zhang *et. al.* for different chalcogens.⁴¹ First, a 0.1 mM $\text{Sb}(\text{OAc})_3$ solution was prepared in a 1:1 ratio by weight of toluene and alkylamine ligand (octylamine, dodecylamine, or oleylamine) by sonicating for 15 minutes. The total mass of solution was 5 g. After sonicating, a stir bar was added, and the supersaturated milky white solution of $\text{Sb}(\text{OAc})_3$ was stirred vigorously. While stirring, 0.5 mL of ammonium sulfide solution (20 wt%, aqueous) was added quickly, making the total sulfur concentration 0.245 mM. The reaction immediately turned a reddish brown, remained turbid, and was stirred for ~ 1 min to ensure a completed reaction. The solution was then transferred directly to a quartz capillary for SAXS characterization of the as-synthesized nanoparticles and their assembly. This synthesis procedure deviates from the methodology of Zhang *et. al.* in key ways that render the process more amenable for commercial scales. First, using a lower concentration (20 wt%) of aqueous ammonium sulfide allows for the direct injection of the sulfur reagent into the antimony acetate solution. We find that, for this material system, additional drying and preparation of the ammonium sulfide precursor into an alkylamine solution is unnecessary. Secondly, the preparation of the cation solution is also performed at room temperature, whereas Zhang *et. al.* specify much more elevated temperatures to ensure complete dissolution of the metal salts, sometimes under nitrogen to prevent oxidation. Conversely, with antimony acetate, we observed an opaque white solution indicating incomplete dissolution. Under these reaction conditions, antimony acetate is prone to oxidize but its sulfurization is still able to proceed (Figure S6). The ability to conduct the entire process in open air, at room temperature, and without drying or intensive preparation of precursors is attractive for commercial production.

4.2.3 Dry Synthesis of Antimony(III) Sulfide Nanoparticles

More closely following Zhang *et al.*,⁴¹ a dried ammonium sulfide solution in octylamine was prepared in open air to be used as the source of sulfur for the room temperature synthesis of ultrasmall Sb_2S_3 nanoparticles. First, 0.8 mL of 40–48 wt% aqueous ammonium sulfide was added to 10 mL of octylamine and stirred. After 15 minutes, activated 3.4 Å molecular sieves were added and allowed to stir for an additional

15 minutes. A 2 mL aliquot of this solution was then injected into the 0.1 mM $\text{Sb}(\text{OAc})_3$ solution which was prepared as previously described with a mixture of 50 wt% octylamine and 50 wt% toluene using 15 min of sonication. Molecular sieves were activated via heating at 110 °C under vacuum for approximately 48 hours.

4.2.4 Scanning Transmission Electron Microscopy

Scanning transmission electron microscopy (STEM) samples were prepared by the drop casting of diluted nanoparticles onto carbon film, 200 mesh nickel grids (Electron Microscopy Sciences; Hatfield, PA). STEM imaging was performed using an aberration-corrected Nion UltraSTEM 100 operated at 60 kV with a convergence semi-angle of 32 mrad. High-angle annular dark field (HAADF) images were acquired using an annular dark-field detector with inner and outer collection semi-angles of 80 and 200 mrad, respectively.

4.2.5 Fourier Transformed Infrared Spectroscopy

Attenuated total reflectance Fourier transformed infrared spectroscopy (FTIR) was performed using a Thermo Fisher Scientific Nicolet IS50R equipped with a diamond window at a resolution of 2 cm^{-1} . Solid nanoparticle samples were dried overnight under vacuum prior to measurement.

4.2.6 X-ray Scattering Sample Preparation and Measurement

Immediately after the previously described synthesis of Sb_2S_3 nanoparticles, the nanoparticle reaction solution was transferred into a quartz capillary. Thin walled ($10\text{ }\mu\text{m}$) 1.5 mm diameter quartz capillaries were purchased from Hampton Research (Aliso Viejo, CA) and were sealed with two part 5-minute epoxy from Devcon (Illinois Tool Works; Danvers, MA). Small angle x-ray scattering (SAXS) was performed on a Xenocs Xeuss 3.0 (Grenoble, France) powered by microfocus GeniX 3D x-ray generator for $\text{Cu K}\alpha$ (0.15406 nm wavelength) and a Dectris EIGER 2 1M x-ray detector. The measurements were made at detector distances of 1.80 m, 0.90 m, 0.37 m and 0.05 m. The 2D images recorded were reduced and merged using XSACT 2.10 from Xenocs (Grenoble, France). Peak positions were determined using Origin 2016 from OriginLab (Northampton, MA).

X-ray diffraction data was acquired using a Bruker D8 Discover Microfocus powder X-ray diffractome-

ter equipped with a Pilatus 100K large-area 2D detector with X-ray source (Cu tube $k\alpha$ radiation 1.54184 Å) operating at 100 mA and 50 kV. Samples were drop-cast onto silicon wafer under ambient conditions.

4.2.7 Preparation of Sb_2S_3 Electrode Material

To prepare an electrode from ultrasmall Sb_2S_3 nanoparticles, the nanoparticles first had to be washed, followed by a ligand stripping procedure. After the reaction, the turbid solution of particles was transferred to a falcon tube with 5 mL of ethanol and centrifuged at 5000 rpm ($2907 \times g$) for 3 minutes before resuspending in toluene. This process was repeated 3 times. To strip the ligands, the NPs were first dispersed in acetonitrile through vortexing and sonication before transferring to a dram vial and stirring vigorously with a stir bar. The acetonitrile is a poor solvent for the alkylamine coordinated NPs, so the solution appeared more aggregated. An autoinjector was used to dispense 2 mL of hydrazine monohydrate (N_2H_4 , 64-65%) into the solution at a rate of 0.025 mL/min over 2 hours. The final volume of the resulting solution was approximately 25 mL and 1 M of hydrazine. As the ligands were stripped by the hydrazine, the NPs sedimented and deposited onto the glass of the dram vial over the course of the process. Once all the NPs had sedimented, the acetonitrile supernatant was discarded, and the deposited particles were dispersed back into a small amount of acetonitrile and nanopure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) in a 1 to 1 ratio using sonication and dried using a rotovap. Qualitatively, the ligand exchange could be deemed successful as polar solvents suspended the nanoparticles more thoroughly than nonpolar solvents after the exchange.

Once dry, the NPs were mixed using an agate mortar and pestle with conductive carbon (Super P) and Sodium carboxymethyl cellulose (Na CMC) dissolved in water at a concentration of 33 mg/mL in a ratio of 64:21:15. This ratio was used following the battery preparation of Kravchyk et. al. using other antimony sulfide nanoparticles.⁹ Once the slurry was homogenous, a $12.7 \mu\text{m}$ (0.5 mil) electrode was coated on copper foil using a stainless-steel doctor blade. The printed electrodes are dried on a heating plate at 80°C then stored in a vacuum oven set to 90°C for >24 hrs until needed. 15 mm electrode punch-outs resulted in an areal electrode loading that ranges from $0.5\text{--}0.8 \text{ mg cm}^{-2}$. Similar loadings were used for fair comparison between the samples.

4.2.8 Electrochemical Characterization

All electrochemical characterization was done in a 2032 coin cell configuration. Coin cells were assembled in an argon-filled glovebox ($O_2 < 1$ ppm, $H_2O < 1$ ppm). For Li-ion, one layer of glass fiber and one layer of polypropylene membrane were used as the separator with 150 μ L of 1 M $LiPF_6$ in EC:DMC (1:1 v/v) with 3 wt% FEC. For Na-ion batteries, one layer of glass fiber separator was used with 100 μ L of 1 M $NaClO_4$ in propylene carbonate (PC) with 3 wt% FEC. Li and Na metals were used as counter electrodes. Electrochemical measurements were performed using a constant current mode for both, charge and discharge between 0.01–2.0 V on a MACCOR (Tulsa, OK) 64 channel Battery Tester.

4.3 Results

4.3.1 Synthesis of Ultrasmall Sb_2S_3 Nanoparticles

The room temperature synthesis of ultrasmall Sb_2S_3 nanoparticles is achieved by dissolving antimony(III) acetate ($Sb(OAc)_3$) in toluene and an alkylamine followed by the fast injection of a 20 wt% aqueous solution of ammonium sulfide, $(NH_4)_2S$, at room temperature under vigorous stirring. The opaque white $Sb(OAc)_3$ solution turns a turbid reddish brown immediately as nanoparticles form (Figure 4.1A). The solution is vigorously stirred with a stir bar for 1 minute to ensure a complete reaction. The formation of a turbid solution and a low-density precipitate, which sediments within a few hours, suggests the presence of large structures within the dispersion. Since the reaction benefits from vigorous stirring, we found octylamine to be most suitable for synthesis as higher melting point alkylamines tend to form a gel following the reaction. To characterize these materials, SAXS was used to probe the ‘as-synthesized’ matrix. Using SAXS, the presence of highly ordered structures within the nanoparticle dispersion was identified (Figure 4.1C). The turbid solution was found to contain long (>300 nm) assemblies in a ‘rod-like’ hexagonal packing, which is easily distinguishable from typical cubic closed-packed structures.^{42,43} The sharpness of peaks, and their magnitude, suggests a strongly scattering medium with a high degree of order. This result, in conjunction with the high turbidity and formation of precipitates, suggests that a mesophase is produced after the reaction.⁴⁴

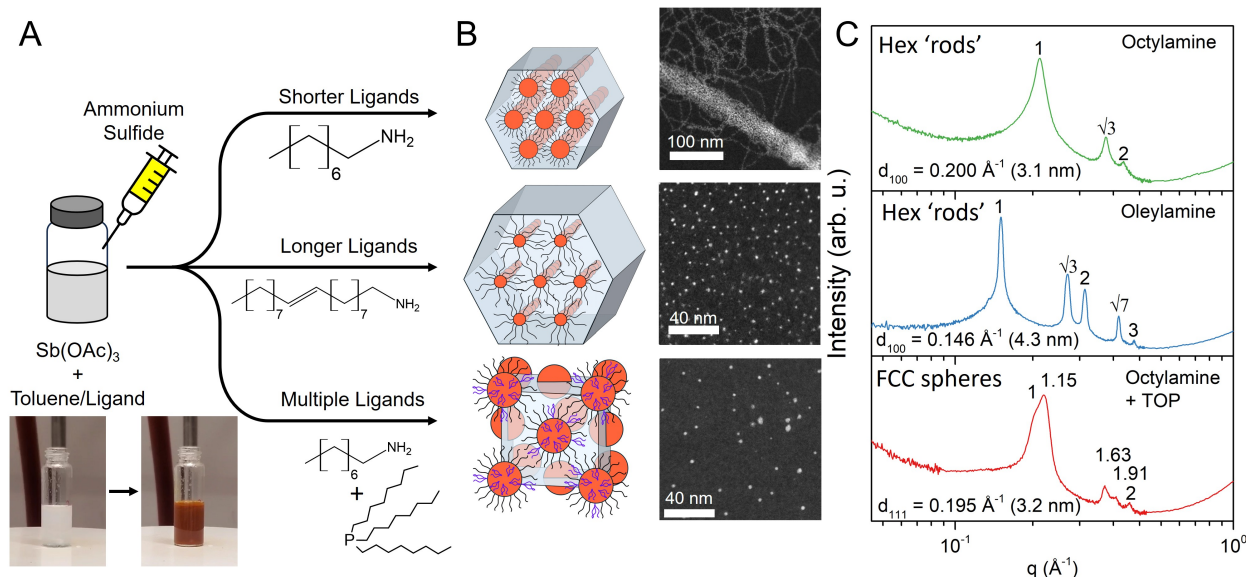


Figure 4.1: Diagram depicting **A)** the room temperature, open air, reaction between antimony acetate ($\text{Sb}(\text{OAc})_3$) and 20 wt% aqueous ammonium sulfide using ligands of different lengths (octylamine and oleylamine) and chemistries (trioctylphosphine) to produce **B)** ultrasmall (3 nm) Sb_2S_3 nanoparticles identified with scanning transmission electron microscopy (STEM) in high-angle annular dark field (HAADF) imaging mode. **C)** Small angle x-ray scattering measurements of the as-synthesized reaction matrix reveals the particles order into a mesophase with tunable arrangements and spacings in the as-synthesized matrix.

The structure of the mesophase of assembled nanoparticles is further controllable by changing the length and functional group of the ligands. Figure 4.1B shows this graphically. Shorter alkylamines, like octylamine, reduce the center-to-center spacing (d_{100}) of the ‘rods’, while longer ligands, such as oleylamine, increase the spacing while maintaining the same hexagonal structure (Figure 4.1C). The spacing in the [100] direction, which is attributed to the position of the first scattering peak, when using a 50 wt% solution of octylamine in toluene was $0.200 \text{ \AA}^{-1}$ (3.1 nm), while an equal weight percent of oleylamine gave spacings of $0.146 \text{ \AA}^{-1}$ (4.3 nm). Given that the spacings are only a few nanometers larger than the extended lengths of the alkylamines, octylamine has an approximate length of 1.0 nm and oleylamine is approximately 2.04 nm long when fully extended,^{45,46} the particles are ultrasmall in all cases (1 - 4 nm) and coordinated by ligands. These particle sizes were confirmed using HAADF-STEM (Figure 4.2-Figure 4.5). The same hexagonal structure is not maintained, however, when 10 wt% of another ligand, trioctylphosphine (TOP), is added in conjunction with octylamine. Instead, the structure becomes a face-centered cubic spherical arrangement with a d_{111} spacing of $0.195 \text{ \AA}^{-1}$ (3.2 nm). The ‘rod-like’ hexagonal organization that is observed for all

pure alkylamine ligands is unusual for spherical particles since there is no obvious driver for assembly into linear arrays.^{30,47,48} From high-resolution aberration-corrected scanning transmission electron microscopy (STEM) in high-angle annular dark field (HAADF) imaging mode, it is determined that the Sb_2S_3 primary particles are ultrasmall, discrete, and roughly spherical. However, depending on the ligand, the particles can also form fibrous structures (Figure 4.2). These fibers are like those previously reported by Nevers *et al.* in syntheses of CdS magic-sized clusters.⁴⁴ These researchers reported a similar hexagonal structure of ultrasmall nanoparticles, and suggest that formation of a mesophase halts the growth of the particles by sequestering nucleation sites away from monomers in the reaction solution. The reaction solution being supersaturated is also thought to be critical in making nucleation more prevalent than growth for this and other ultrasmall systems.^{49,50} Still, the exact cause for the stability during formation of particles in this size regime is debated.²⁷

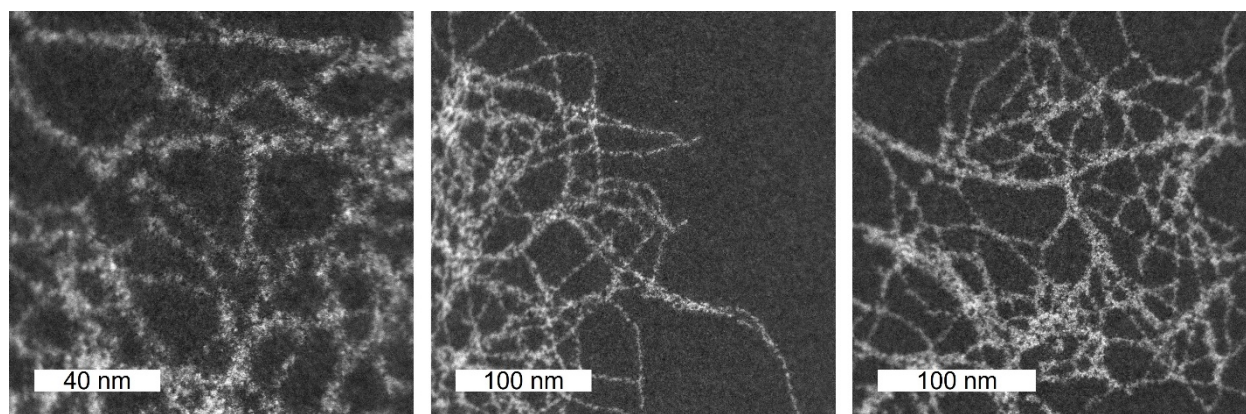


Figure 4.2: HAADF-STEM images of ultrasmall antimony sulfide nanoparticles synthesized in a 50/50 wt% solution of octylamine and toluene from $\text{Sb}(\text{OAc})_3$ (0.1 mM) and ~ 0.5 mL 20 wt% aqueous $(\text{NH}_4)_2\text{S}$.

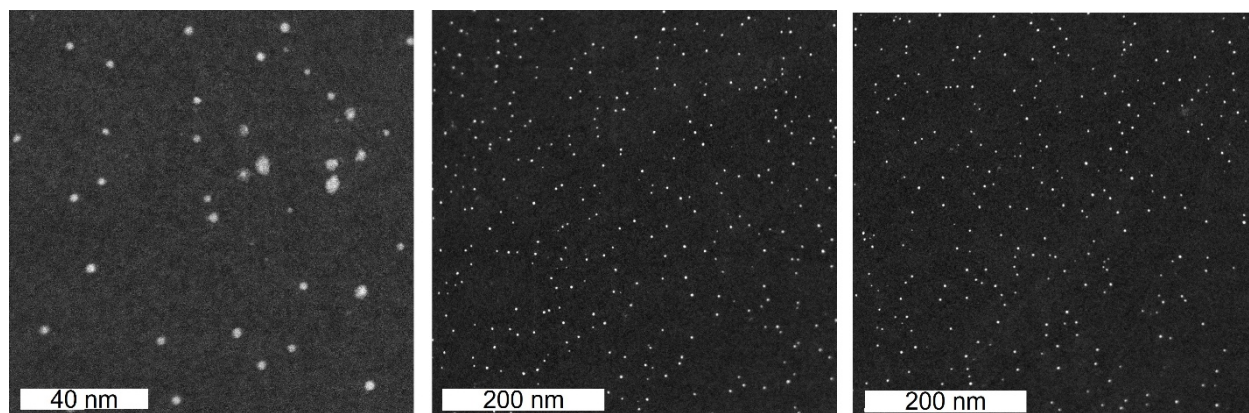


Figure 4.3: STEM images of ultrasmall antimony sulfide nanoparticles synthesized in a solution containing 40 wt% octylamine, 10 wt% trioctylphosphine, and 50 wt% toluene. Size of 2.6 ± 0.7 (N=641).

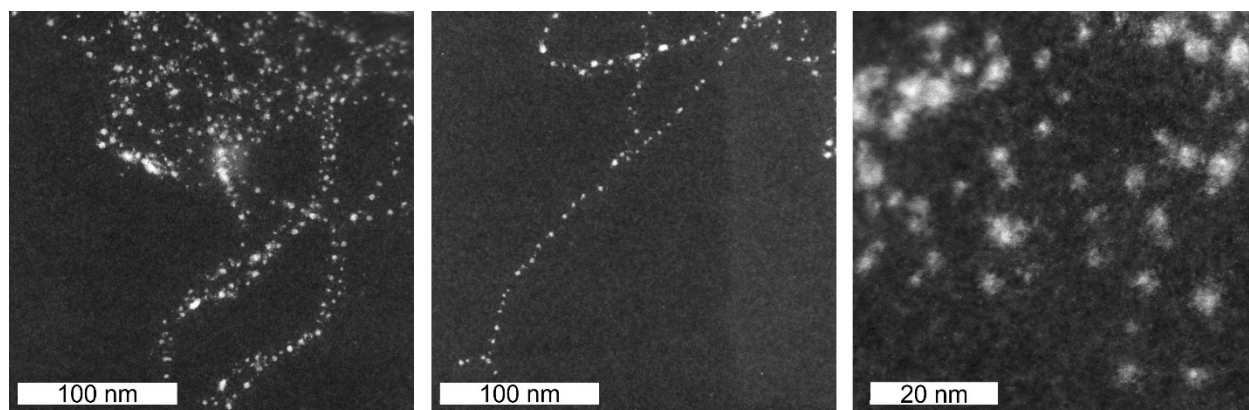


Figure 4.4: STEM images of ultrasmall antimony sulfide nanoparticles synthesized in a 50 wt% solution of dodecylamine. Size of 3 ± 1 nm (N=260).

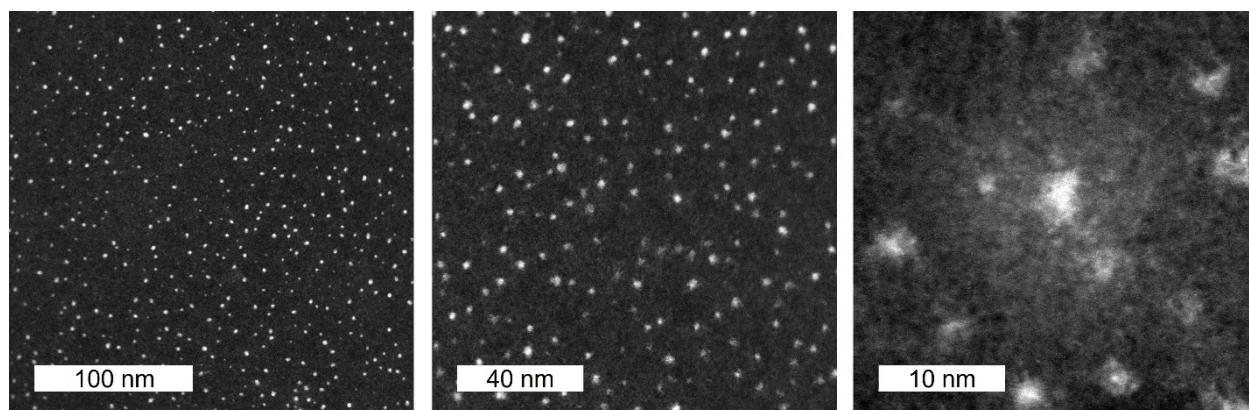


Figure 4.5: STEM images of ultrasmall antimony sulfide nanoparticles synthesized in a 50 wt% solution of oleylamine. Size of 2.5 ± 0.5 nm (N=764)

The synthesis reported in this work produces similar particles when using other alkylamines, namely dodecylamine and oleylamine. However, a fibrous morphology was not observed in HAADF-STEM (Figure 4.4, Figure 4.5) for these samples. Primary particles were not found to be crystalline, and lattice fringes were not distinguishable in HAADF-STEM in any sample. While HAADF-STEM can provide information on the morphology of the primary particles, SAXS is a preferable technique for characterizing assembly since it can probe the structures in the dispersed state without the need for solvent removal. In contrast, morphologies are anticipated to be altered by preparation of samples for imaging due to washing steps required to remove excess ligands and the requisite evaporation of the solvent. This is commonly seen in other nanoparticle systems where the solvent is a critical component to the assembly, and drying disrupts the structure.^{44,51–53}

In this system, the concentration of reagents contributed greatly to the presence of the ‘rod-like’ mesophase, since lower concentrations of $\text{Sb}(\text{OAc})_3$ led to no assembly in solution (Figure 4.6B). When $\text{Sb}(\text{OAc})_3$ was in excess (at high concentrations of Sb^{3+} or low concentrations of S^{2-}) a cubic antimony(III) oxide phase (senarmontite, PDF #98-002-0076) was observed in the wide-angle x-ray scattering (WAXS) range. Since all steps in the synthesis were performed in open air, oxide formation is expected when excess Sb^{3+} is left unreacted. We also note that, in a typical synthesis (Figure 4.6A), there is a single peak in the WAXS region at $2.21 \text{ \AA}^{-1}$ (0.28 nm). While a single peak is insufficient to assign it to be the bulk orthorhombic phase of Sb_2S_3 (stibnite, PDF# 98-000-0411), it is within the approximate range of lattice spacings of layered bulk stibnite.⁵⁴ This indicates that while particles may be too small to be accurately called ‘amorphous’, they do not show evidence of strong crystallinity. Regardless of the choice of ligand, no variations are observed in the position of this WAXS feature between Sb_2S_3 samples. These results are corroborated using x-ray diffraction which can observe higher q values and angles in 2θ (Figure 4.7).

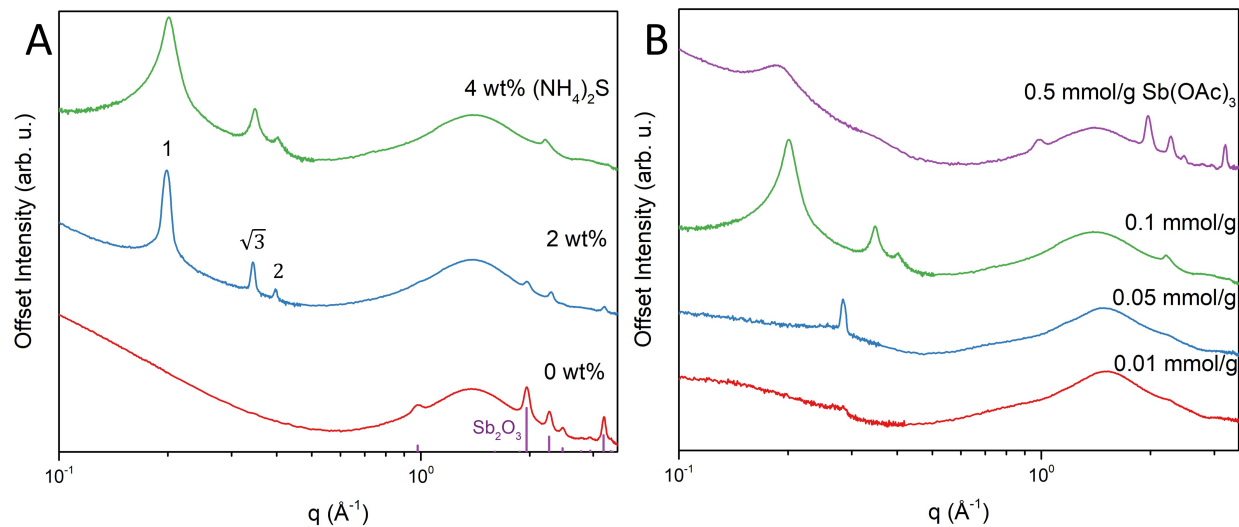


Figure 4.6: SAXS spectra of syntheses in solutions of 50 wt% Octylamine and 50 wt% toluene with increasing concentrations of **A)** 20 wt% aqueous ammonium sulfide $(\text{NH}_4)_2\text{S}$. The reference peaks in the WAXS region belong to orthorhombic senarmontite (Sb_2O_3 , PDF #98-002-0076). This antimony oxide species does not form when ammonium sulfide is in excess. **B)** Syntheses with increasing concentrations of antimony(III) acetate $\text{Sb}(\text{OAc})_3$ in solution. The same Sb_2O_3 species is present when the concentration of $\text{Sb}(\text{OAc})_3$ is above 0.1 mmol/g. Both axes are in log scale.

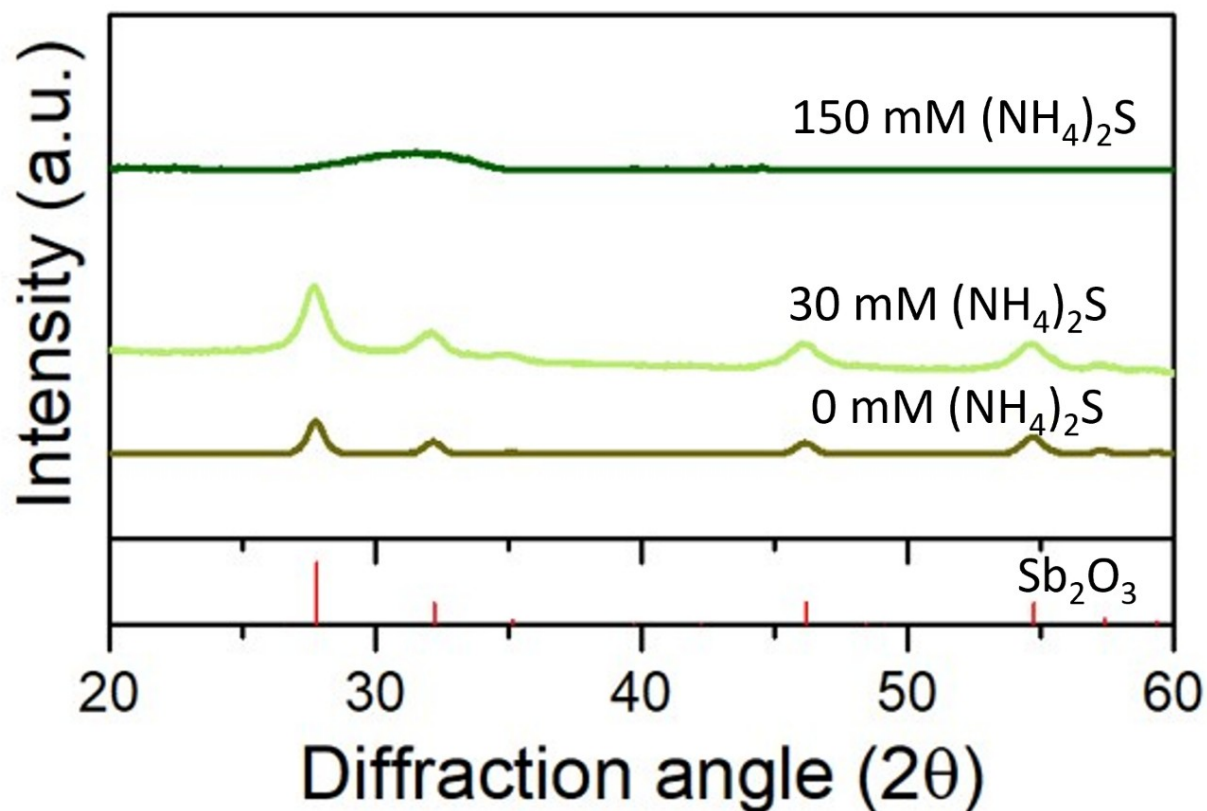


Figure 4.7: X-ray diffraction plots of Sb_2S_3 synthesized using $\text{Sb}(\text{OAc})_3$ in a 1:1 solution of toluene:oleylamine and increasing concentrations of ammonium sulfide $((\text{NH}_4)_2\text{S}$, 20wt% aq.). As the ammonium sulfide concentration increases, more of the $\text{Sb}(\text{OAc})_3$ reacts which reduces oxide formation post reaction. Reference in red is cubic antimony(III) sulfide (senarmontite, PDF #98-002-0076).

4.3.2 Structure of Self-Assembled Nanoparticle Mesophases

In addition to synthesizing ultrasmall Sb_2S_3 nanoparticles, the spacings in the hexagonal ‘rod-like’ packing were shown to be controllable by changing the length and concentration of alkylamine ligands. Three different ligands were evaluated for variations in length: octylamine (8 carbons), dodecylamine (12 carbons), and oleylamine (18 carbons) (Figure 4.8A). The shortest ligand, octylamine, produced the closest packing with a center-to-center spacing of 3.1 nm. Dodecylamine and oleylamine are substantially longer ligands and produce spacings of 3.7 and 4.3 nm respectively. All alkylamine samples shared the same signature Bragg spacings of hexagonal close-packed ‘rods’ with peaks at scattering vectors of q , $\sqrt{3}q$, $2q$, and $\sqrt{7}q$ corresponding to d_{hk0} lattice spacings d_{100} , d_{110} , d_{200} , and d_{210} respectively.⁴² The peak position in q -space

(q) is converted to real-space (d) by the relationship $d = 2\pi/q$ where q is in units of inverse length.⁵⁵ The longest ligands produced the narrowest peaks, which is indicative of a uniform structure containing large domains in the scattering medium.⁵⁶

The lattice spacings were also tuned by adjusting the concentration of the alkylamine ligand in the solution. In these syntheses, the ligand was replaced with the same mass of toluene over the workable range. For octylamine (Figure 4.8B), the syntheses ranged from no added ligand (0 wt%), to pure octylamine (90 wt% of the total mass including precursors). When no ligand was added, the Sb_2S_3 particles deposited immediately onto the walls of the vial as it was unstable in solution without a ligand. Lower concentrations of octylamine gave larger particle spacings and broader peaks while higher concentrations produced tighter spacings and narrower peaks.

Nanoparticles prepared from longer ligands displayed similar trends. The spacing for dodecylamine (Figure 4.8C) and oleylamine (Figure 4.8D) assemblies change over a 0.2 nm and 0.3 nm range respectively as the ligand concentration is altered. The variation was proportional to the total number of carbons in the alkyl chain. While octylamine produced sharper features on increasing concentration, dodecylamine and oleylamine showed the sharpest features at ~50 wt% ligand before broadening again above 70 wt%. An added complication, which was unique to dodecylamine, was that high concentrations of the ligand precipitated to form crystalline lamellar phases. This produced smaller peaks in the SAXS data that increased in intensity with increasing concentration of dodecylamine at ratios of 1q ($0.271 \text{ \AA}^{-1}$, 2.3 nm) and 2q (marked with an asterisk in Figure 4.8C).⁵⁷ No lamellae were observed below 20 wt%, and no peak shift was observed between 50 and 70 wt% ligand.

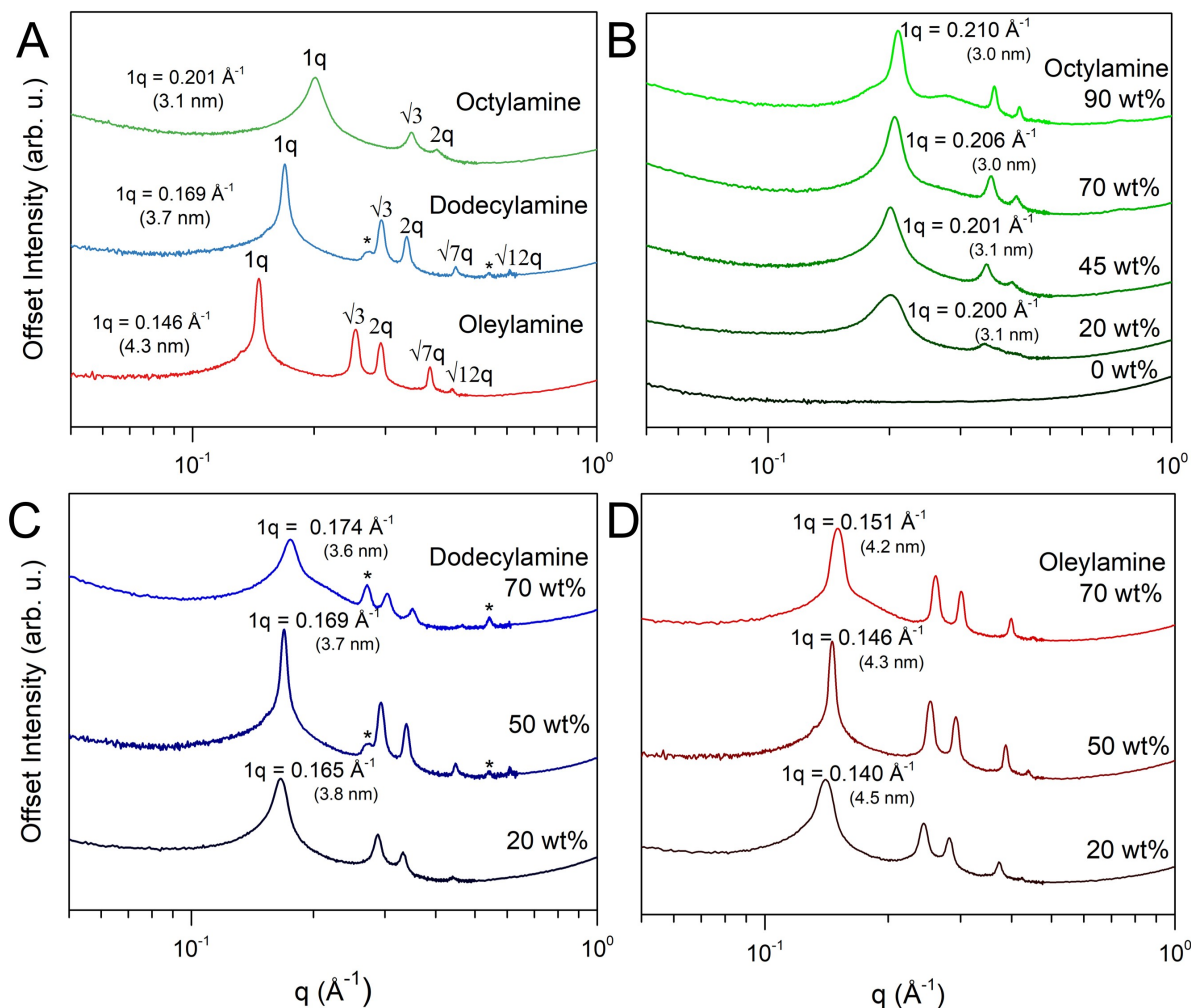


Figure 4.8: SAXS profiles for Sb_2S_3 syntheses using **A)** 50 wt% solutions of three alkylamines with a range of chain lengths. Syntheses were performed with these three alkylamines, **B)** octylamine, **C)** dodecylamine, and **D)** oleylamine with variable concentrations ranging from 20 wt% to 70 wt% or more. In dodecylamine samples, lamellae formed when the ligand was not fully dissolved. These follow a peak spacings of $1q$ (at $0.271 \text{ \AA}^{-1}$) and $2q$. Both are marked with an asterisk. All axes are in log scale.

Since this synthesis procedure involved the addition of an aqueous reagent ($\sim 0.5 \text{ mL}$ of aqueous 20 wt% $(\text{NH}_4)_2\text{S}$) to a nonpolar organic solution ($\sim 5 \text{ mL}$ toluene and alkylamine), the potential influence of water on the structure of the assembly was determined. SAXS data was collected on samples synthesized with octylamine at different concentrations, while also preparing corresponding backgrounds by centrifuging each sample at 10,000 RPM ($5,814 \times g$) and collecting the supernatant, absent of particles, for measurement (Figure 4.9A). SAXS showed the hexagonal ‘rod-like’ structure for as-synthesized samples, while the

corresponding background only shows a broad feature that shifts to higher angles ($0.21 \text{ \AA}^{-1}$ to $0.28 \text{ \AA}^{-1}$) as the concentration of octylamine increases. This feature may result from the spacing between reverse micelles of solvated water molecules. To demonstrate that this feature is independent of the assembly of nanoparticles, we followed a procedure by Zhang *et al.* for transferring and drying aqueous ammonium sulfide into a liquid alkylamine using $3\text{\AA}$ molecular sieves.⁴¹ Details for the procedure can be found in the methods section. Both samples in Figure 4.9B were prepared with 1:1 octylamine to toluene by weight. Two samples were prepared following this procedure: one that was dried with molecular sieves and a control that had no molecular sieves. SAXS was collected for both along with a corresponding background prepared by centrifugation and separation of the supernatant (Figure 4.9B). In both the dried sample with sieves and the control without sieves, the ‘rod-like’ hexagonal structure is still maintained while the intensity of the broad feature belonging to solvated water decreases. Since the same hexagonal mesophase is obtained using both ‘dry’ (Figure 4.9B) and ‘wet’ methods (Figure 4.9A), assembly involves primarily Sb_2S_3 particles and ligands. Thus, it is independent from water introduced into the system.

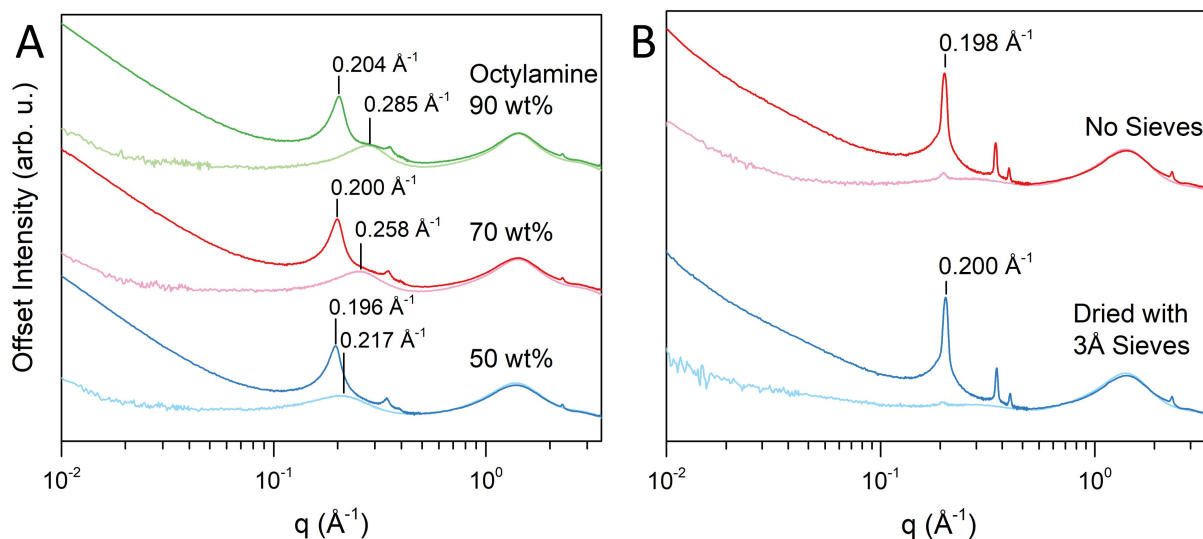


Figure 4.9: SAXS of control samples where **A)** the synthesis of Sb_2S_3 nanoparticles using 90, 70, and 50 wt% of octylamine (dark lines). The nanoparticles assemble into hexagonal ‘rod-like’ arrangement and the d_{100} peak shifts with higher concentrations of octylamine. Background scattering of the solvents (lighter lines) were collected on the centrifuged supernatants of the same samples. **B)** SAXS of control syntheses comparing drying of the aqueous ammonium sulfide into pure octylamine. One (blue) was dried with molecular sieves and the other (red) followed the same procedure of transferring the $(\text{NH}_4)_2\text{S}$ (aq.) to octylamine, but no sieves were added. Both axes are in log scale.

4.3.3 Altering Nanoparticle Self-Assembled Structure with Multiple Ligands

Ultrasmall Sb_2S_3 particles, which are expected to be homogeneously covered in ligands, do not assemble into the typical spherical particle packing of face-centered cubic or body-centered cubic. Instead, they assemble into hexagonal arrangements typical for rods or wires.^{42,58,59} Based on the sharpness of the peaks, the assemblies are expected to be highly ordered. Since particles remain un-sintered however, they are also sufficiently stabilized by alkylamine ligands. Similar hexagonal assemblies of ultrasmall nanoparticles, or clusters, have been described by Nevers *et al.* for CdS magic-sized clusters.⁴⁴ A possible explanation for this in the Sb_2S_3 system is that alkylamine ligands form a non-uniform coating despite lacking strong internal crystallinity. Since alkylamines are an L-type ligand with a demonstrated preference for cation-rich facets,^{60,61} it is possible for Sb_2S_3 clusters to form a non-uniform coating on the particle. In this work however we do not experimentally confirm the coverage of ligands given the difficulty of this task due to the small size and low contrast of the particles.

To explore this possibility, syntheses in octylamine were performed with increasingly higher concentrations of another ligand, trioctylphosphine (TOP). The amount of nonpolar solvent, toluene, remained constant while octylamine was replaced with TOP. TOP was added to the reaction just before injecting the sulfur reagent, $(\text{NH}_4)_2\text{S}$. This prevented Sb^{3+} from being preferentially solvated by TOP, which might have slowed the kinetics of the reaction due to TOP's bulky alkyl tails. SAXS on samples with variable TOP concentrations from 0 to 10 wt% (Figure 4.10A) show a continuously variable structure. As the TOP fraction increases, the 'rod-like' hexagonal assembly shifts to a face-centered cubic (FCC) spherical packing. The FCC phase is identified by reflections at ratios of $1q$, $\sqrt{4/3}q$, $\sqrt{8/3}q$, $\sqrt{11/3}q$, and $2q$ for the [111], [200], [220], and [222] directions respectively.^{62,63} The gradual shift occurs with an increase of the [220] FCC peak, which becomes noticeable above 0.5 wt% TOP, as well as the splitting of the first peak into the [111] and [200] FCC reflections. A possible explanation for this behavior is that the trioctylphosphine is less nucleophilic than octylamine and therefore does not bind with as much site specificity. This would more fully coat the particle in ligands as more anion and cation sites would be passivated. As opposed to mostly cation sites when only octylamine is used. To confirm this mechanism in future studies, ab initio simulation and more thorough spectroscopy would be required to determine the exact binding site of the amine and phosphine ligands.

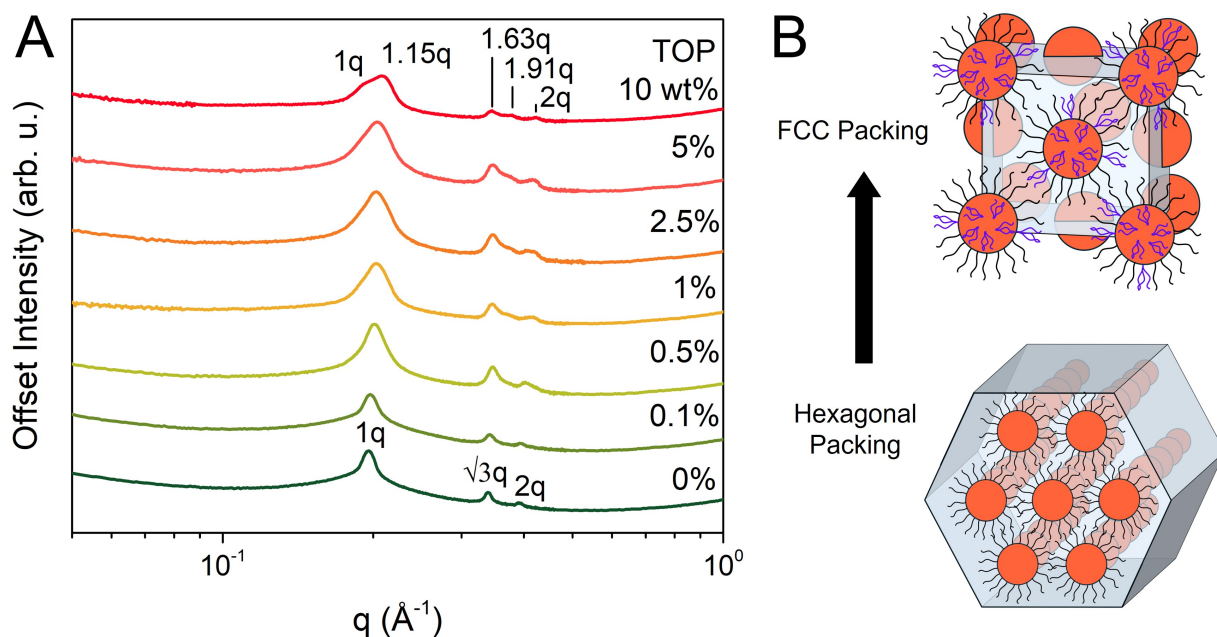


Figure 4.10: A) SAXS data of syntheses where octylamine was replaced with increasing amounts of TOP in solution which coincides with the structure transitioning from a hexagonal arrangement to an FCC structure. The FCC phase can be identified by the growth of the [220] peak ($1.91q$) and the splitting of the hexagonal structures' [100] peak into the [111] and [200] peak ($1q$ and $1.15q$ respectively). B) Graphic demonstrating the structure using only alkylamine ligand (black) and the increased axial spacing resulting in FCC packing using an addition of TOP (purple) to cover the surface.

4.3.4 Ligand Exchange

Since long alkyl groups are highly insulating,⁶⁴ it is necessary to remove them before preparing the Sb_2S_3 nanoparticles into electrodes. To do this, a ligand exchange procedure was followed using hydrazine, which has been shown to be an effective displacing agent for alkylamines on metal chalcogenides.^{9,65} Nanoparticle samples were characterized in SAXS before (Figure 4.11A) and after (Figure 4.11B) the washing and ligand exchange procedure. After performing the ligand exchange, the assemblies of the nanoparticles were disrupted, and the particles deposited onto the glass vial. Once exchanged, the SAXS curve only features a single broad peak at $0.35 \text{ \AA}^{-1}$ (1.8 nm), which is expected to represent the center-to-center distance between hydrazine coordinated nanoparticles of this size.

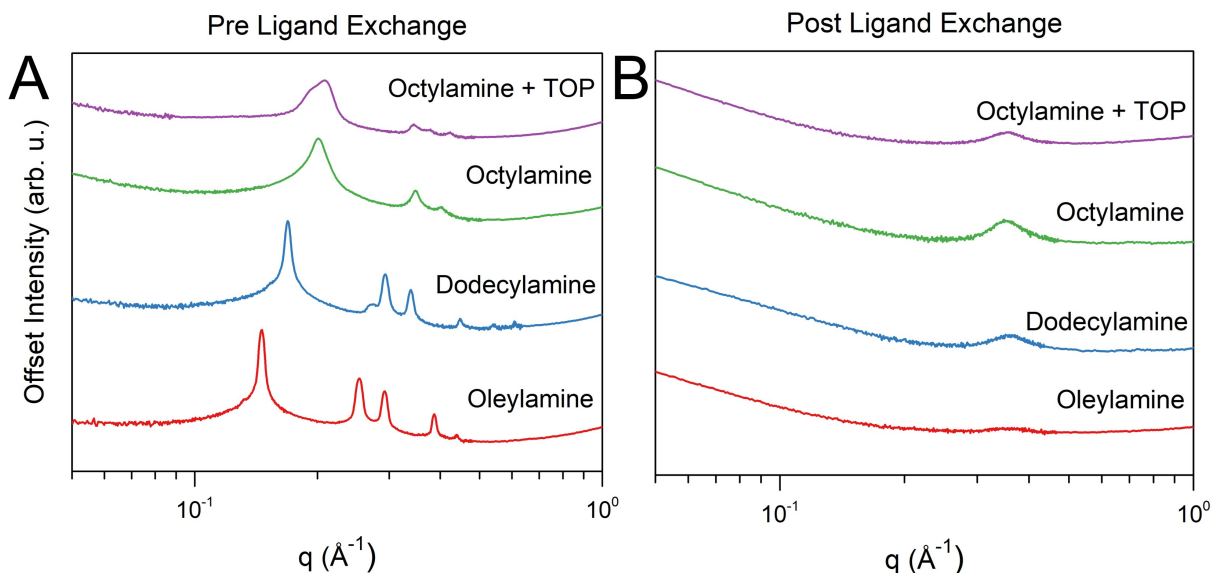


Figure 4.11: SAXS spectra of **A)** Sb_2S_3 particles before ligand exchange synthesized with oleylamine, dodecylamine, octylamine, as well as octylamine with 10wt% trioctylphosphine (TOP). **B)** After synthesizing, the particles were washed and ligand exchanged with hydrazine (procedure in methods) before being dispersed in water and characterized in SAXS. Both axes in log scale.

In addition to SAXS, successful ligand exchanges were confirmed through Fourier-transformed infrared spectroscopy (FTIR) (Figure 4.13). After ligand exchanging, the C-H bend peaks found between 3000 and 2850 cm^{-1} greatly decreased in intensity or disappeared in all samples regardless of choice of ligand.⁶⁶ The Sb_2S_3 nanoparticles can also be identified in the FTIR spectra. Characteristic Sb_2S_3 vibrational peaks at 721 cm^{-1} and 538 cm^{-1} are present,⁶⁷ as well as a peak characteristic of the metal-sulfide interaction at 1376 cm^{-1} .⁶⁸ Furthermore, the identity of the nanoparticles is confirmed with EDS (Figure 4.14-Figure 4.17) which demonstrates that before and after the ligand exchange the particles remain antimony(III) sulfide. These images also show that the aggregate size is not easily characterized in imaging techniques as the history of the sample's preparation plays a significant role in the size and morphology of secondary particle formation.

4.3.5 Electrochemical Performance

All electrode preparation, battery assembly, and electrochemical characterization was performed by co-author Dr. Guesang Lee.

The electrochemical performance of ultrasmall Sb_2S_3 nanoparticles as negative electrodes for Li^+ and Na^+ ion batteries was evaluated.⁶⁹ To ensure consistency and reproducibility, the electrode slurry composition, slurry preparation, electrode fabrication, and testing environment using a coin cell configuration were standardized. The only variable in these experiments was the choice of ligand (at 50 wt% in solution) during the nanoparticle synthesis prior to ligand exchange. For clarity, although the ligands are stripped, each sample is referred to by the ligand that was used during the sample's synthesis.

Figure 4.12A shows the redox peaks of ultrasmall Sb_2S_3 from lithiation and delithiation in the form of total differential capacity data. All samples exhibit distinct lithiation peaks between 1.2–1.5 V vs. Li^+/Li , corresponding to the solid electrolyte interphase (SEI) formation and the conversion reaction (Equation 4.1). In the two electrodes prepared from nanoparticles synthesized in octylamine with 10 wt% TOP (Oct-TOP) as well as dodecylamine, a shoulder forms before the primary peak indicating intermediate reactions preceding the SEI formation. A second reduction peak at ~0.85 V represents the alloying reaction (Equation 4.2).^{7–9,40,70} During delithiation, a broad oxidation peak near 1.0 V reflects the de-alloying of Li-ions from antimony. This is followed by a shallow peak between 1.5–2.0 V, attributed to the reverse conversion reaction.⁹

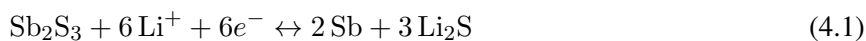


Figure 4.12B presents the charge-discharge profiles of the first cycle obtained at 0.3 A g^{-1} , a rate slow enough to capture detailed redox processes and the energy contributions of individual reactions. The lithiation profiles show distinct plateaus corresponding to the SEI formation, conversion, and alloying reactions, consistent with the total differential capacity peaks shown in Figure 4.12A.⁸ Notably, most of the irreversible capacity occurs above 1.2 V, which is evident from the difference in the total differential capacity data of the first and second cycle. As stated earlier, this region with the stark difference between the first and second cycle is primarily associated with SEI formation and initial conversion reactions.

Discharge capacities were highest for Oct-TOP at 1980 mAh g^{-1} , followed by oleylamine at 1816 mAh g^{-1} .

g^{-1} , octylamine alone at 1481 mAh g^{-1} , and dodecylamine at 1412 mAh g^{-1} . The subsequent charge capacities were approximately half of the first discharge capacities, consistent with irreversible SEI formation and side reactions in nanostructured materials, especially considering the high surface to volume ratio of these nanoparticles.

Other antimony sulfide nanocrystals in literature have exhibited an impressive specific capacity of 643 mAh g^{-1} (61% retention) when charged and discharged at a current of 12 A g^{-1} .⁹ In our work, the ultrasmall Sb_2S_3 nanoparticles demonstrated similar rate capabilities, particularly for Oct-TOP, which had a capacity of $\sim 700 \text{ mAh g}^{-1}$ at 12 A g^{-1} , corresponding to 67% retention of its capacity measured at 0.3 A g^{-1} . Oleylamine had the next highest with 561 mAh g^{-1} (61% retention), while dodecylamine and octylamine exhibited similar capacities with 510 and 521 mAh g^{-1} , respectively (67% retention for both). With increasing current, less energy from the conversion reaction contributes to the overall capacity. This is due to the relatively large band gap (4.8 eV) of Li_2S , which is a major reason why lithium-sulfur batteries often have limited charging speed.⁷¹⁻⁷³ This also explains the 20% decrease in retention compared to that of antimony nanocrystals when fast charging/discharging.³⁹

To assess the lifetime of the electrode, the electrodes were cycled at a relatively fast rate of 2.4 A g^{-1} until their capacity retention dropped to 50%. As shown in Figure 4.12D, which shows the capacity data up to 500 cycles, the initial discharge capacities varied noticeably among the four electrode samples, reflecting differences in irreversible side reactions, including the SEI formation. The electrode prepared with Oct-TOP demonstrated the highest initial capacity at 1177 mAh g^{-1} , followed by oleylamine (1014 mAh g^{-1}), dodecylamine (648 mAh g^{-1}), and octylamine (375 mAh g^{-1}).

As expected, capacity decreases over time, but the variations in the rate of decrease between samples is apparent, with Oct-TOP reaching 67% retention at the 500th cycle (80% at the 370th cycle). Similarly, both octylamine and dodecylamine exhibited a gradual capacity decrease. Once the capacity reached 597 mAh g^{-1} for octylamine, it slowly degraded, whereby at the 500th cycle it showed 77% retention (80% at the 480th cycle). With dodecylamine, once the capacity reached 541 mAh g^{-1} , the capacity decreased to 55% retention (80% at the 318th cycle). As for oleylamine, similar to the cycle life data shown with previously showcased Sb_2S_3 nanoparticles prepared using oleylamine as the coordinating ligand, the capacity degraded until the 380th cycle upon which it plateaued around 50% capacity retention (80% at the 167th cycle).⁹

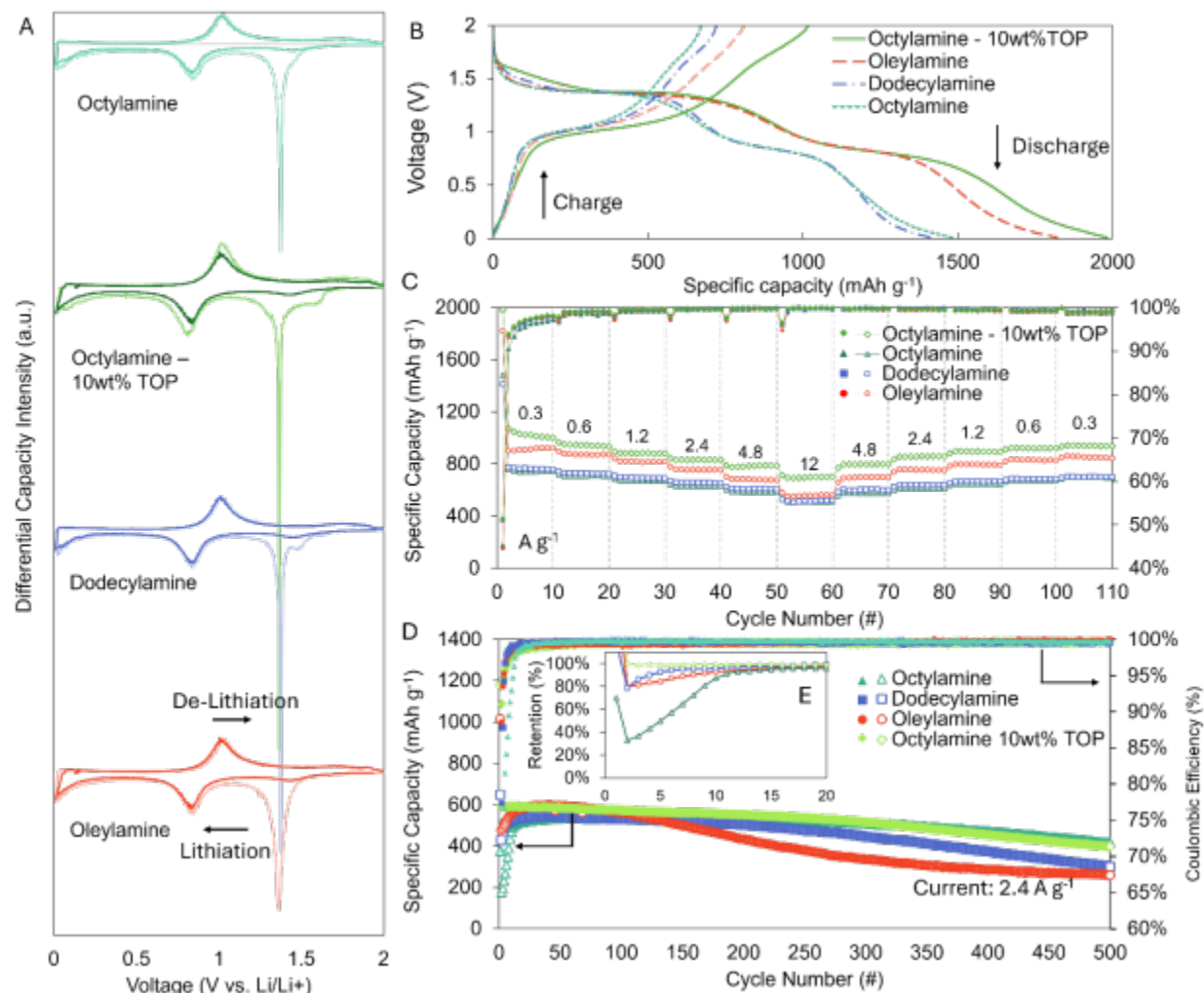


Figure 4.12: Li-ion electrochemical data of the ultrasmall Sb_2S_3 synthesized in different ligating environments. **A)** Total differential capacity data of the first (lighter) and second (darker) cycle for nanoparticles synthesized using the identified alkylamine. **B)** Galvanostatic charge-discharge curves of the first cycle. **C)** Rate capacity. **D)** Cycling stability data. **E)** Normalized cycling stability data of the first 20 cycles.

Altogether, this work shows that the ultrasmall Sb_2S_3 nanoparticles performed the best when synthesized in a solution of 50 wt% toluene, 40 wt% octylamine, and 10 wt% trioctylphosphine (Oct-TOP). Over 500 cycles at 2.4 A g^{-1} , Oct-TOP experienced a similar drop in specific capacity to octylamine, but exhibited excellent rate capability, outperforming all other samples. When adding TOP, the SEI layer formation appears to be impacted as is evidenced by the slight difference in shape of the galvanostatic lithiation/delithiation curves between the Oct-TOP and octylamine samples as seen in Figure 4.12B. Additionally, the Oct-TOP sample required fewer initial cycles to reach its maximum capacity. All other samples exhibited a gradual

capacity increase during the initial cycles. Eventually, each stabilized at 537 mAh g⁻¹ for octylamine, 541 mAh g⁻¹ for dodecylamine, and 597 mAh g⁻¹ for oleylamine. This suggests the importance of the synthesis procedure and packing behavior regardless of whether the initial ligating environment has been removed. The synthesis path or mechanism could be important factors to consider especially for particles in this size regime that self-assemble.

Even among the three other alkylamines, there were distinct disadvantages that were identified with using longer ligands despite all producing similar nanoparticles and following a complete ligand exchange procedure. One possibility for these electrochemical differences is the assembly's affect on the formation of secondary nanoparticles during the ligand exchange where the largest aggregates form. A more open arrangement of particles might allow for better ion diffusion into the larger aggregates. While this is difficult to assess through imaging, as the aggregates are microns in size while the spaces between particles are only a few nanometers, the surface area is a better indicator. A higher surface area would indicate if the arrangement of the ultrasmall nanoparticles exposes more of the particle surface to the electrolyte. Brunauer-Emmett-Teller (BET) analysis was used to characterize the surface area of nanoparticles synthesized with the four ligands. The octylamine-TOP sample was measured to have the highest surface area at 33 m² g⁻¹, followed by octylamine at 22 m² g⁻¹, and then dodecylamine and oleylamine at 13 and 12 m² g⁻¹ respectively.

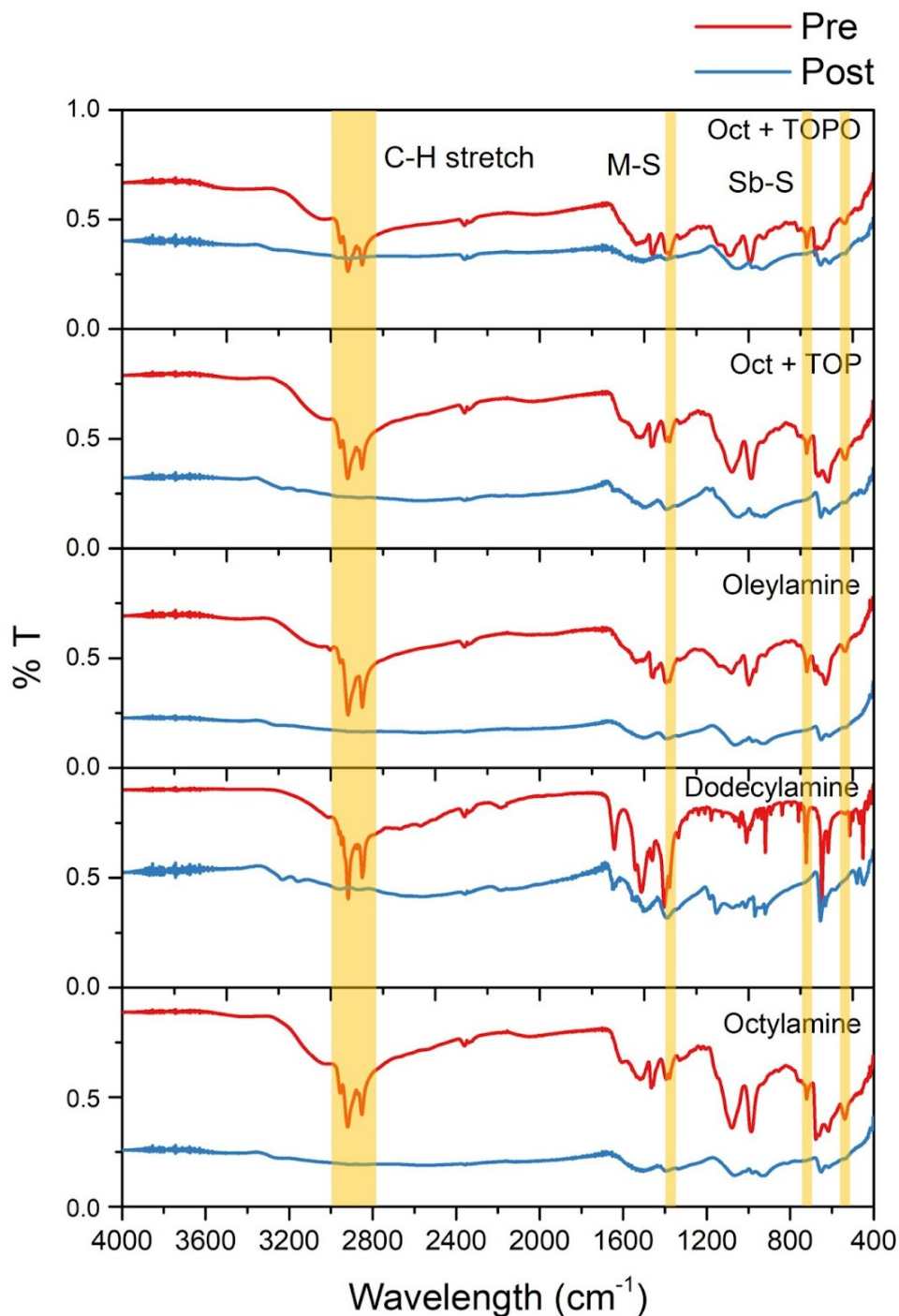


Figure 4.13: Attenuated transmission reflectance Fourier transformed infrared spectra (ATR-FTIR) of washed samples of ultrasmall Sb_2S_3 nanoparticles synthesized with the indicated ligands before (red) and after (blue) performing the ligand exchange procedure detailed in the methods section. The C-H stretches between $3000\text{--}2800\text{ cm}^{-1}$ is characteristic of each of the long chain ligands and is highlighted yellow. Also highlighted in these samples is the characteristic metal-sulfide interaction (1376 cm^{-1}) and Sb-S vibrational modes (721 cm^{-1} and 538 cm^{-1}).

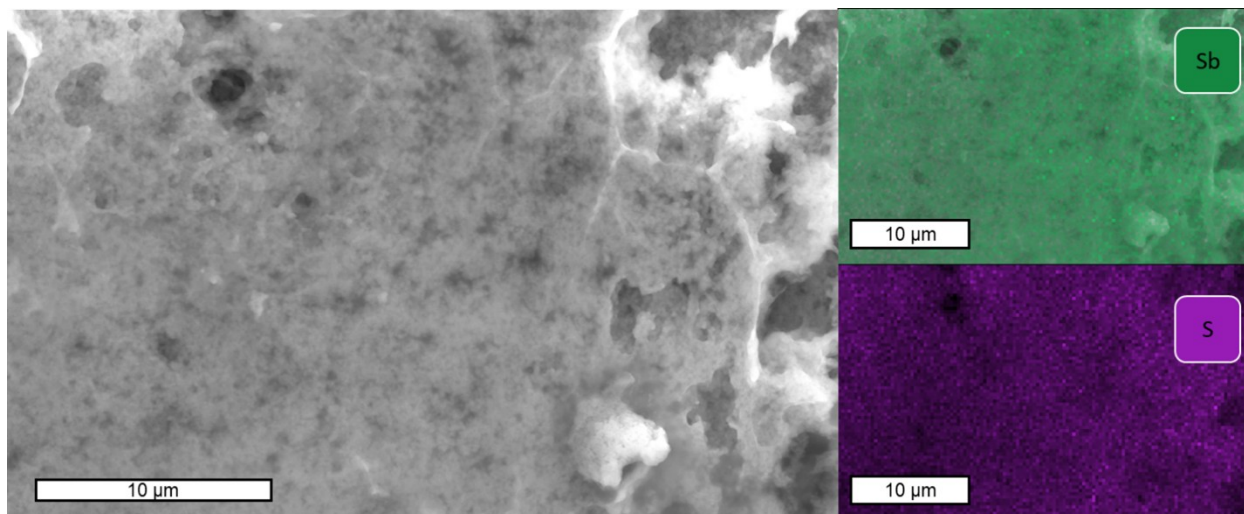


Figure 4.14: SEM image of dried Sb_2S_3 nanoparticles synthesized with octylamine before ligand exchange and washing on a carbon TEM grid with EDS maps of antimony and sulfur.

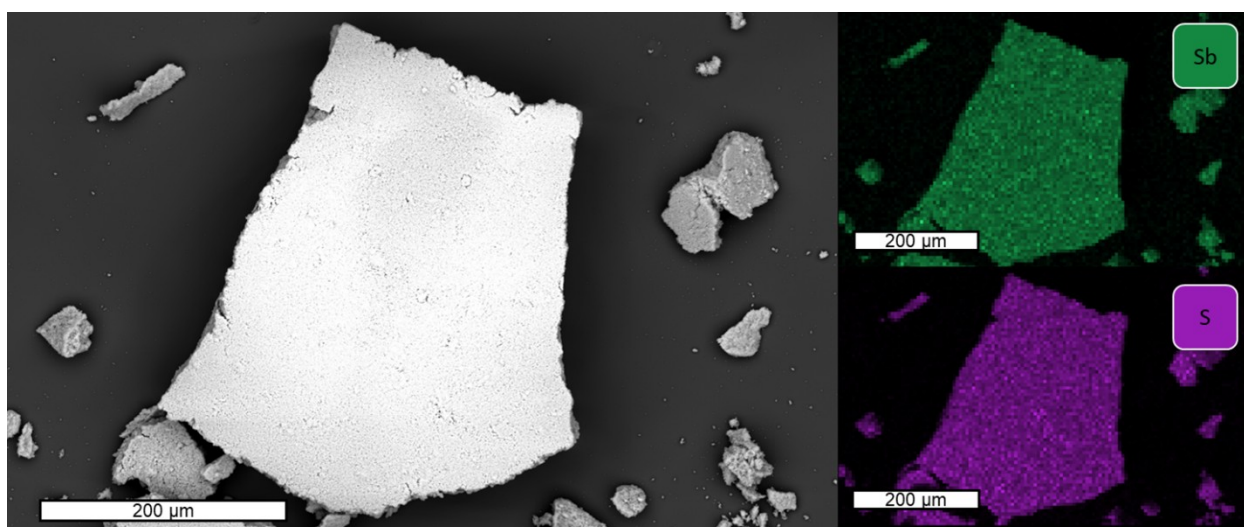


Figure 4.15: SEM image of dried Sb_2S_3 nanoparticles synthesized with octylamine after ligand exchange and washing on a carbon TEM grid with EDS maps of antimony and sulfur.

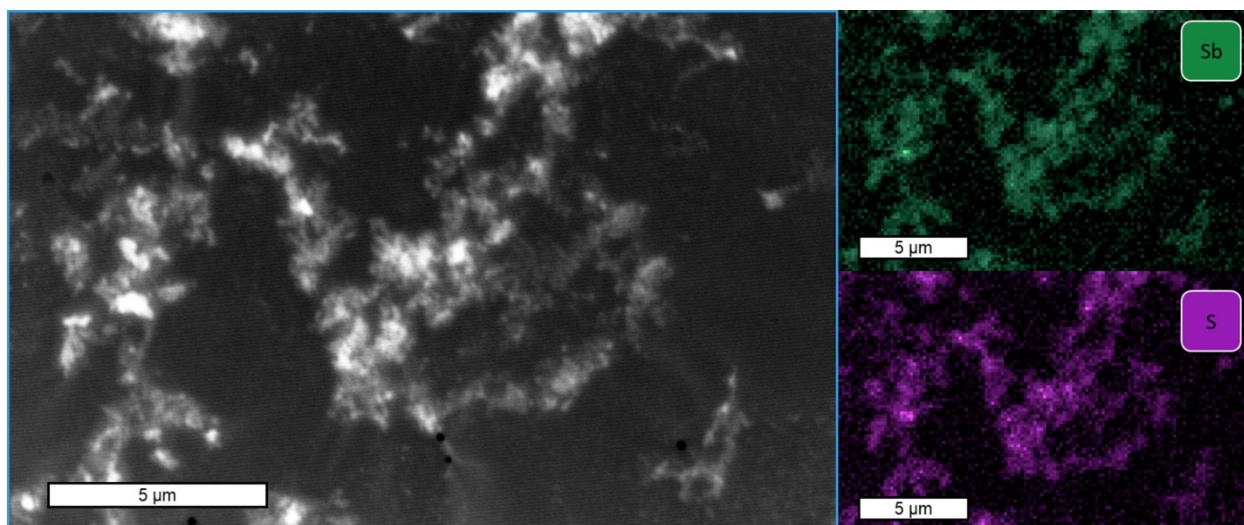


Figure 4.16: SEM image of dried Sb_2S_3 nanoparticles synthesized with octylamine and trioctylphosphine before ligand exchange or washing on a carbon TEM grid with EDS maps of antimony and sulfur.

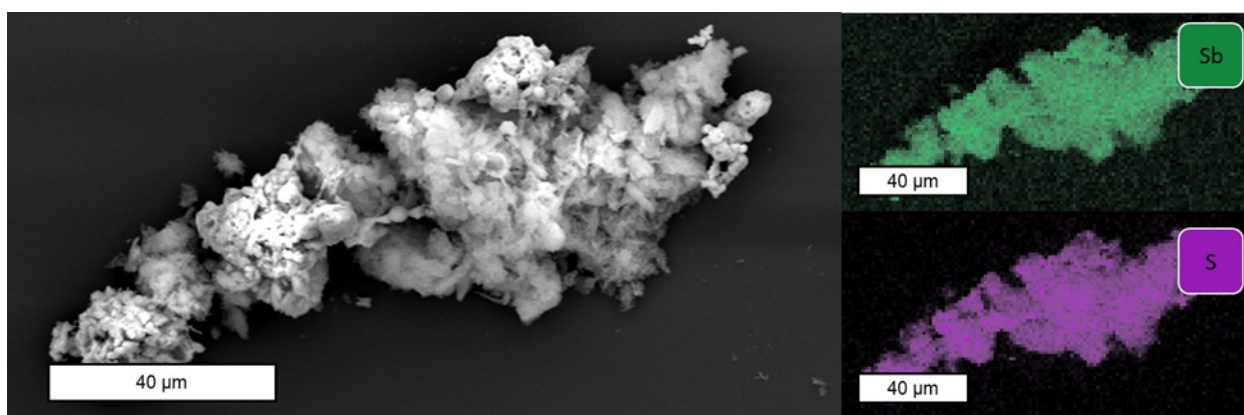


Figure 4.17: SEM image of dried Sb_2S_3 nanoparticles synthesized with octylamine and trioctylphosphine after ligand exchange or washing on a carbon TEM grid with EDS maps of antimony and sulfur.

4.4 Discussion

Assembly is a commonality between many systems with ultras-small building blocks.^{27,50,74} It is often attributed to strong registry along preferred crystallographic directions, which can be followed by sintering.^{28,33,75,76} In this work, the Sb_2S_3 particles lack strong atomic lattice spacings and remain unsintered (Figure 4.2-Figure 4.5). This indicates that the particles are aligning *via* well-coordinated ligands. While the length of the ligands affects the distance between the particles, the concentration of ligands in solution

also affects the spacing to a lesser extent. As the concentration of ligands increases, the interparticle spacing decreases (Figure 4.8). At lower ligand concentrations, when the solution is mostly toluene, the ligands on the surface extend since nonpolar toluene is a ‘good solvent’ for nonpolar alkyl groups. When the solution has a much higher concentration of ligand, the ligand contracts on average since the nonpolar alkyl group is not as strongly solvated.^{31,77} This effect also explains the narrowing of the peaks in the octylamine series (Figure 4.8A) where the structure of the assembly becomes more homogeneous as the ligands contract and spacing decreases.

In all Sb_2S_3 nanoparticles synthesized with alkylamines, the packing was ‘rod-like’ and hexagonal (Figure 4.8). Only when trioctylphosphine (TOP) was added did the packing change to a close packed face-centered cubic arrangement (Figure 4.10). We postulate that this is due to the primary particles being more fully covered by ligands given that trioctylphosphine would bind with less site-specificity.^{60,78} In addition, it has been shown that trioctylphosphine readily oxidizes to form trioctylphosphine oxide when used in open-to-air reactions.⁷⁹ Trioctylphosphine oxide coordinates preferentially into cation vacancies as an electron acceptor,⁸⁰ making it more likely to fully cover the Sb_2S_3 particles in conjunction with alkylamines, electron donating L-type ligands. In control experiments, the addition of 10 wt% trioctylphosphine oxide also resulted in the FCC structure (Figure 4.18).

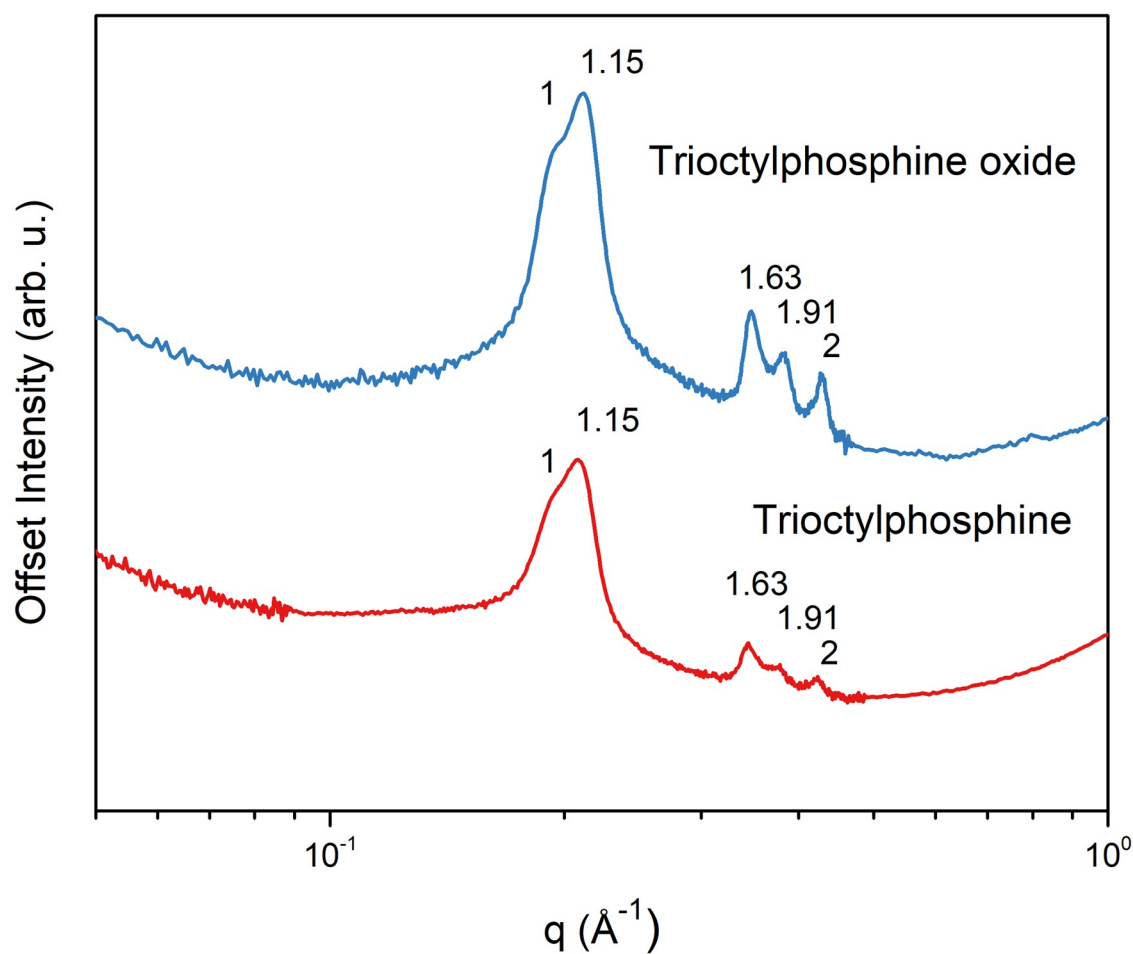


Figure 4.18: SAXS plot comparing a synthesis performed using 10 wt% trioctylphosphine oxide and 10 wt% trioctylphosphine both with octylamine as a co-ligand that show nanoparticle assemblies in the same FCC packing. Both axes in log scale.

The effect that different alkyl phosphine or amine ligands might have on a ligand exchange is rarely discussed in literature as it relates to ultrasmall particles or electrochemical applications. In this work, the length of the alkylamine ligand is inversely proportional to the overall performance of the battery, where smaller ligands improve cycling and specific capacities even after a complete ligand exchange was performed.⁶⁹ The addition of trioctylphosphine was also found to improve specific capacity and reduce or eliminate the number of cycles needed to reach a more stable capacity. The phenomenon of increasing capacity over the first few initial cycles is commonly referred to as activation cycling. It is attributed to

the gradual rearrangement of the active material, conductive medium, and binder into a more kinetically favorable configuration.^{81–83} Activation cycling is often more pronounced in systems where nanoparticles are highly bridged or aggregated into secondary particles.⁸² Since the trioctylphosphine containing sample requires fewer, or no, activation cycles, it suggests that the particles are in a more favorable arrangement before cycling. In a half-cell configuration with a plentiful lithium reserve from a lithium metal counter electrode, this behavior may seem minor. However, in a full-cell configuration with balanced capacities in the negative and positive electrodes, capacity may fade due to repeated exposure of active materials to the electrolyte, reducing the benefits of high energy density materials. Even if the positive electrode mass is increased or an active material like lithium iron oxide (Li_2FeO_3) is used to compensate for SEI layer growth, the overall battery capacity would still be limited.

We postulate that the variances in the battery data, including differences in capacity degradation behavior, may result from size and morphology differences in the aggregated particles after ligand exchange. The higher surface area of the Oct-TOP sample measured with BET would support a difference in secondary particle morphology resulting in a higher surface area which may be an explanation for its difference in electrochemical performance compared to the other samples. Unfortunately, the ligand exchange strategy used in numerous past studies,^{9,22,39,65,84} typically involving redispersing the material in a solvent of opposite polarity with a chosen ligand, lacks the necessary details to definitively determine the cause. Post-analysis often only highlights differences in chemical structure before and after ligand exchange using techniques such as attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy.^{3,9,39,66,84} This work also demonstrates that the majority of the alkyl chains were effectively removed (Figure 4.13). Nonetheless, the battery data reveals differences in electrochemical performance in various aspects. We believe the variations in secondary particles stem from factors during and after the synthesis such as the assembly and packing density of the nanoparticles before and during the ligand exchange.

4.5 Conclusion

The synthesis of ultrasmall antimony(III) sulfide (Sb_2S_3) particles is reported using a room temperature, open-air procedure. Self-assembly of ultrasmall nanoparticles is characterized *via* small angle x-ray scattering, showing the formation of elongated hexagonal structures typically found in rod-like particles and

micelles. This assembly is modified by adjusting the ligands and/or the solvent, with longer ligands, as well as lower concentrations of ligand in solution, increasing the interparticle spacing. The unusual hexagonal structure is proposed to be caused by a non-uniform coordination of alkylamines over the Sb_2S_3 surface. Using an additional ligand (trioctylphosphine), which lacks in binding selectivity, leads to the formation of an FCC phase. The performance of Sb_2S_3 nanoparticles in Li^+ battery electrodes is exceptional, demonstrating over 500 cycles above 80% retention, as well as cycling up to 12C with a relatively small drop in capacity. The ligand used in the nanoparticle synthesis is also shown to impact the performance of electrodes even after a ligand exchange. This suggests that ligand identity is an important design criterion that cannot be overlooked regardless of how similar the final nanoparticle morphology may appear. This project demonstrated an effort towards improving the stability of lithium ion batteries in high power applications like transportation or power tools. Improving the lifetimes of these devices serves to limit the number of battery replacements that are needed, lowering demand, and keeping them out of landfills. Ultrasmall Sb_2S_3 also is a substitute for graphite in the Li^+ battery anode. Graphite is a critical material due to its difficulty to produce and recycle. This work then functions twofold in meeting the overarching objective of improving sustainability in the critical materials sector.

4.6 References

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Chapter 5

Exploring Crystallization with Reaction-Diffusion Coupling in Hydrogels

5.1 Chapter Introduction

The transition to clean, renewable sources of energy will ultimately become a material problem. The production of clean energy using wind turbines, solar panels, and even nuclear reactors requires many times more minerals than traditional fossil fuels, and storing that energy in electrochemical cells is also mineral-intensive.¹ Electric vehicles and the batteries that power them will become a major driver of demand for many of these minerals, such as cobalt, nickel, lithium, and manganese.¹ These, among many other materials, are often termed critical materials because of the threat that the destabilization of their supply chains could pose to the energy economy.² The issue, however, is not necessarily the abundance of these materials in the earth's crust, but rather the economic viability of extracting them from sufficiently concentrated sources.^{3,4} For example, around 54% of the world's supply of cobalt is extracted from the Democratic Republic of the Congo (DRC), yet it is the 30th most abundant element in the earth's crust, after copper at the 26th place for reference.^{5,6} Many countries have therefore identified cobalt as a critical material because of the risk of exposure created by sourcing so much of the world's supply of an essential element from a single region.⁷ Diversifying the supply chain is important in cases with such exposure to disruption, but opening new mines is not always desirable. Both because it is often economically infeasible and because

of the environmental costs of expanding areas for mining.^{7,8} More extensive recycling of spent devices and materials, however, promises to aid in supply-chain diversification while also preventing valuable materials from exiting the economy.

Among separation technologies, one of the more desirable processes is simple precipitation. Energetically cheap,^{9,10} sequentially precipitating elements out of a mixed feedstock is a scalable and economically feasible method. As a technology, however, it is significantly held back by a lack of selectivity between elements with similar properties. Cobalt and nickel, for instance, share nearly identical divalent ionic radii and aqueous chemistries, so they readily co-precipitate and are notoriously difficult to separate cleanly by precipitation alone.^{11,12} It is possible, however, to direct a precipitation reaction toward a desired outcome, whether by carefully tuning solubility through the solvent composition,¹³ or by adding ligands that stabilize certain species over others.^{14,15} Many of these strategies can improve selectivity in separation methods based on hydrometallurgical precipitation. If a more complete picture of these classes of reactions can be painted, we will improve our ability to engineer recycling and synthesis methodologies.

Regardless of the method, the parameter space for these reactions is vast. Reactions depend on the concentration and chemistry of the reagents, on additives in solution, and on cooperative, non-linear effects between each component of the solution matrix.^{16,17} High-throughput methodologies have become invaluable for probing these large parameter spaces, owing to their ability to replicate a large number of conditions across the reaction space.^{18–20} One drawback of many high-throughput, autonomous methods, however, is that they typically sample only the end state of the precipitation. Crystallization is, however, a dynamic process of evolving atomic structures and morphologies, with much more to be learned by investigating pathways *in situ* over time. Current methods for investigating crystallization *in situ* are typically not high-throughput; a small number of isolated conditions are usually studied at high resolution, rather than sampling the broader reaction space.^{21–24}

Reaction-diffusion coupling in hydrogels is a useful tool for generating a large space of reaction conditions.^{25–28} In the simplest example, an outer electrolyte containing the first reagent, or a mixture of reagents, diffuses into a gel that has been prepared with an inner electrolyte that would spontaneously precipitate upon reaction with the outer electrolyte. The combination of two well-behaved phenomena, the diffusion and reaction of solvated species, can produce extremely non-linear behavior that pushes reactions far from

equilibrium.²⁹ For over a hundred years, the non-linear behavior of reaction-diffusion systems has fascinated scientists through the formation of phenomena such as the periodically precipitated bands known as Liesegang rings, observed both in gels and in natural rock formations.²⁹⁻³¹ More recently, reaction-diffusion coupling has been examined as more than a phenomenological curiosity. Control of the bands in periodic precipitation reactions has made it possible to predict, fine-tune, and regulate their spacing over long distances, moving us closer to engineering advanced devices using nothing but simple precipitation reactions.³²⁻³⁶ Additionally, reaction-diffusion in hydrogels is being used to synthesize tunable nanostructures, where the position within the gel dictates the conditions of the reaction and the shape of the crystal products.^{25,28} Most relevantly, reaction-diffusion coupling in hydrogels has been demonstrated as an effective separative method, in which a mixed feedstock diffuses into the gel, reacts with the inner electrolyte, and undergoes sequential precipitation of its constituent ions.^{37,38} Both the synthesis and the separation rely on the fact that every position in the gel becomes a unique, dynamic supersaturation environment, resulting in a different reaction outcome at every position. This produces a swath of morphologies to choose from during synthetic campaigns, and creates a sufficiently large number of theoretical stages to produce a separative effect in many mixed-ion outer electrolytes. However, hydrogels suffer from a significant drawback: it is challenging to efficiently study the evolution of crystallization *in situ* as the products develop. Traditional imaging and elemental analyses involve sectioning the gel, which is time-consuming. To investigate the temporal and spatial dependence of crystallization, then, *in situ* techniques such as small-angle X-ray scattering are well suited to probing the structure and morphology of the crystals.^{39,40}

In this work, we conduct ultrasmall-, small-, and wide-angle X-ray scattering on hydrogels prepared with dibasic potassium phosphate while an outer electrolyte of concentrated cobalt(II) chloride diffuses and precipitates. This produces a wide library of morphologies for the cobalt(II) phosphate system, and the X-ray scattering measurements allow us to determine the morphology and crystal structure *in situ* for a large number of samples throughout a column of gel and over long periods of time. Probing the reaction space in this way is remarkably efficient. Restricting mass transport to purely diffusive conditions also allows us to observe crystallization in an atypical regime, which is important for drawing conclusions about the driving forces in this and any other system. Because we have removed convective mixing, we are able to determine that the crystallization of cobalt(II) phosphate proceeds *via* dissolution and reprecipitation

rather than aggregation, a pathway that was previously unknown for this system.²³ This work was done in collaboration with Joelle V. Scott, Abdul Moez, Jingcong Chen, Elias Nakouzi, David S. Bergsman, and Lilo D. Pozzo.

5.2 Experimental

5.2.1 Materials

All chemicals were used as received. Cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$; reagent grade), dibasic potassium phosphate (K_2HPO_4 ; $\geq 98\%$), tribasic potassium phosphate (K_3PO_4 ; $\geq 98\%$), acrylamide ($\geq 99\%$), N,N'-methylenebisacrylamide (BAAM; $\geq 99\%$), and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP; $\geq 95\%$) were purchased from Sigma-Aldrich. Poly(ethylene glycol) diacrylate, 20k g/mol (PEGDA) was purchased from Polysciences (Warrington, PA) and agarose (molecular biology grade) was purchased from Fisher Scientific.

5.2.2 Sample Preparation

Polyacrylamide and PEGDA gel preparation

Both the polyacrylamide and poly(ethylene glycol) diacrylate (PEGDA) gels were prepared as aqueous solutions with 0.15 wt% of lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP), based on the total mass of the sample, as the photoinitiator to generate free radicals for polymerization. Each gel was prepared in a brown dram vial by mixing aqueous stock solutions of either PEGDA or polyacrylamide and crosslinker with photoinitiator, counter ion (if necessary), and additional water to achieve the desired weight fraction. The counter ions were prepared at the desired molarity with respect to the mass of water, not the mass of the total solution which included the mass of polymer. After all solutions were added to the vial in a dark room, the solutions were vortexed and allowed to stand undisturbed until any bubbles had dissipated. The solutions were then dispensed into a 4 inch (103.5 mm) Wilmad-LabGlass™ thin walled high-throughput NMR tube, 5 mm OD (Fisher Scientific), using a long glass pipette and rubber bulb. This was done carefully to avoid bubbles and gel on the walls of the tube above the gel line. The NMR tubes were chosen for their regularity in thickness between tubes to aid sample-to-sample comparisons in scattering data.

For the PEGDA gels, the PEGDA weight percent in the final solution ranged from 5 to 20 wt%. In lower Mw PEGDAs (≤ 4000 g/mol), K_2CO_3 and K_2HPO_4 tended to visually disrupt the gel matrix as the gels turned an opaque white indicating large scatterers were present in the samples.⁴¹ In some cases, especially when using K_2CO_3 and NaOH as counter ions at concentrations above 0.1 M, some molecular weights of PEGDA were not fully gelled after photocuring; at least 15 wt% PEGDA was needed for these solutions to gel properly. A sample was determined to be sufficiently gelled if, when inverted, it maintained its shape and if it could support the addition of a solution to the top of the gel without mixing. Any sample that did not fully gel was excluded from this study.

For the polyacrylamide gels, N,N'-methylenebisacrylamide (BAAm) was used as a crosslinker, such that the concentration of monomer (wt% T) included both polyacrylamide and BAAm, with the crosslinker reported as a percent of the total monomers (% C). Equation 5.1 shows the calculation for the total percentage of monomer (polyacrylamide plus BAAm) where m_a is the mass of polyacrylamide, m_C is the mass of crosslinker, m_T is the total mass of the aqueous solution. The concentration of crosslinker is calculated with Equation 5.2 where %C is the percent of monomer that is crosslinker. The polyacrylamide weight percent varied between 7.5 wt% T and 5%C.

$$\text{wt\% T} = 100 \frac{m_A + m_C}{m_T} \quad (5.1)$$

$$\%C = 100 \frac{m_C}{m_A + m_C} \quad (5.2)$$

Agarose gel preparation

Agarose gels were prepared by heating an aqueous stock solution of 2 wt% agarose to approximately 95°C. The stock solution was dispensed into pre-warmed vials of water and counter ion (K_2CO_3 , K_2HPO_4 , NaOH). These were then vortexed, and warmed back to 95°C before dispensing into the sample container. The gels were then allowed to cool down to room temperature.

5.2.3 Diffusion Measurements

Using a Nikon D5600 camera body with a Nikon AF-S DX Micro Nikkor 40 mm (f/2.8G) lens and intervalometer, images of samples were taken every 5 minutes after the addition of the outer electrolyte to the

top of the gel. A ring light and white background were used to image the samples. The samples were held upright by a printed PLA stand, and were covered using the provided plastic cap. Using the OpenCV Python package, each frame of the video had the color of the precipitant isolated using a hue, saturation, and value (HSV) mask. A contour was drawn around the masked area using a parameterized box of least area. The width of the box, converted to centimeters, was extracted from every frame of the timelapse.

5.2.4 X-ray Scattering Measurements

ultrasmall-, small-, and wide-angle X-ray scattering (USAXS) experiments of reaction-diffusion samples were performed using the USAXS instrument at Advanced Photon Source, Argonne National Laboratory, beamline 12-ID-E.^{42,43} The combined q -range was between 1×10^{-4} to $0.3 \text{ \AA}^{-1}$ for USAXS (3×10^{-5} to $0.3 \text{ \AA}^{-1}$ for high-resolution USAXS), 0.03 to $1.3 \text{ \AA}^{-1}$ for SAXS, and 0.8 to $6 \text{ \AA}^{-1}$ for WAXS; here $q = 4\pi \sin(\theta)/\lambda$, where λ is the wavelength and θ is one half of the scattering angle. The X-ray energy for standard USAXS/SAXS/WAXS was 21 keV ($\lambda = 0.5904 \text{ \AA}$). X-ray photon flux was approximately $5 \times 10^{12} \text{ mm}^{-2}\text{s}^{-1}$ in standard USAXS operation and $1 \times 10^{12} \text{ mm}^{-2}\text{s}^{-1}$ in high-resolution USAXS. Combined USAXS/WAXS measurements had a time resolution of 3.5 min per run. Samples consisted of hydrogels between 1 and $20 \text{ wt\%}$ in 5 mm OD Wilmad-LabGlass high throughput NMR tubes (Fisher Scientific) held in place by an ad hoc PLA printed holder.

Hydrogel samples were prepared for SAXS/WAXS at the University of Washington by preparing the gel in the same manner as described previously, but transferred into a resin printed cartridge stage with 1 mm Kapton (polyimide) film walls in the beam path and photopolymerized using a UV lamp (365 nm). SAXS/WAXS was performed on a Xenocs Xeuss 3.0 (Grenoble, France) powered by microfocus GeniX 3D X-ray generator for $\text{Cu K}\alpha$ ($1.5406 \text{ \AA}^{-1}$ wavelength, 8.05 keV) and a Dectris EIGER 2 1M X-ray detector. The measurements were made at detector distances of 1.80 m , 0.90 m , 0.37 m and 0.05 m . The 2D images were reduced and merged using XSACT 2.10 from Xenocs (Grenoble, France).

5.2.5 SEM Imaging

Scanning microscopy images and energy dispersive spectroscopy elemental maps of samples were taken using a Thermo Fisher Scientific Phenom Pharos G2 SEM-STEM desktop instrument. Reaction-diffusion

gel samples were prepared by extracting and dissecting the gel while still hydrated into 2 mm thick cross sections. The polyacrylamide and agarose gel samples were soaked in ethanol to remove the metal chloride solution and desiccate the gel samples before drying under low vacuum at room temperature. PEGDA gel samples were soaked in water to remove chloride salts and desiccated in a vacuum oven. The dried gel cross sections were fixed to a standard aluminum pin stubs using double sided carbon tape with aluminum base and 5 mm width (Electron Microscopy Sciences; Hatfield, PA).

5.3 Results

5.3.1 Optical Diffusion Measurements

In these experiments, the reaction-diffusion front, or propagation front, is the position of the first visible precipitants in the gel column. The outer electrolyte is the aqueous solution of metal ions that is placed on top of the column of gel while the counter ions are the reagents solvated in the gel itself. Often times in reaction-diffusion literature, the ions dissolved into the gel are referred to as the inner electrolyte and the ions on top of the gel are the outer electrolyte.⁴⁴ In every reaction-diffusion system, the choice of inner and outer electrolyte and the rate of reactivity between them greatly influences the observed phenomena.^{45–47} Cobalt(II) chloride and dibasic potassium phosphate react quickly to form a highly insoluble ($K_{sp} \approx 10^{-35}$), reddish-pink solid.⁶ As this precipitation reaction proceeds, and CoCl_2 (outer electrolyte) diffuses through the gel, the K_2HPO_4 (inner electrolyte) is consumed at the propagation front. Figure 5.1A shows this graphically. This produces a counter-diffusion of the K_2HPO_4 in the opposite direction of the CoCl_2 . The concentrations of the reagents with respect to both time and position throughout the gel are therefore complex and dynamic. Each infinitesimal slice of the gel column can be treated as a unique time-dependent series of supersaturation conditions. As the propagation front proceeds, the CoCl_2 concentration will steadily rise while the K_2HPO_4 concentration decreases as fast as it can be transported to the reaction front.

The position of the reaction-diffusion front can be tracked using time-lapse photography and simple computer vision. In this method, the colorful precipitate is isolated from the colorless gel and white background, which works best when the reaction product is strongly colored compared to the gel. Regular time-lapse images (5 min apart) were taken for the duration of the reaction, and using OpenCV (opencv-

python),⁴⁸ an HSV (hue, saturation, and value) threshold was applied to the images that separated just the colored precipitant. A bitwise mask was applied, and the dimensions of the mask for each image were measured in pixels using a rectangle of least area (Figure 5.1B). This was plotted and converted to distance over time. The positions over time were then fit with the mean-square displacement equation for 1D displacement (Figure 5.1C) according to Fick's law or Brownian motion in 1D (Equation 5.3) where $x_f(t)$ is the position of the front with respect to time, t is time, and P_f is the effective propagation rate of the front.⁴⁹

$$x_f(t) = \sqrt{2P_ft} \quad (5.3)$$

Whether a reaction-diffusion process in a hydrogel is non-Fickian is not so easy to say.^{50,51} The time law, $x_n^2 \propto t_n$,⁵² and modifications of it,⁵³ which relate the velocity of the propagation front to time, are commonly used for modeling Liesegang phenomena. This remains accurate when the hydrogel is static,⁵⁴ and has a relatively low weight fraction.⁵¹ The reaction-diffusion process is well fit by Equation 5.3, and the weight fraction of the PEGDA gels is 10 wt% in these diffusion measurements, so the 1D mean-square-displacement was determined to be a reasonable model for an effective propagation rate. In reality, it is not necessary to

To model the reaction-diffusion process inside the gel, we utilize the 1D diffusion equation (Equation 5.4) where D_i is the molecular diffusivity of the cobalt and phosphate species. We assume an irreversible reaction of the form $3 \text{Co}^{2+} + 2 \text{PO}_4^{3-} \longrightarrow \text{CO}_3(\text{PO}_4)_2$ with a reaction term of $r = kC_{\text{Co}}^3C_{\text{PO}_4}^2$.

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial C_i}{\partial x} + r_i \quad (5.4)$$

The system of PDEs was solved numerically in Python using the Radau method. The code can be found in appendix A.1 along with a more detailed description. Five concentrations of K_2HPO_4 (0.04 to 0.2 M) in 700 Mw PEGDA were simulated and measured experimentally (Figure 5.1D). The effective propagation rate of the front was plotted against the concentration of K_2HPO_4 . The measured effective propagation rate and the modeled effective propagation rate differed by a factor of $\alpha = 0.186$ when using literature molecular diffusivities, resulting in the simulated effective propagation rates of the propagation front being half an order of magnitude faster than reality. This was expected as the literature molecular diffusivities are faster than the molecular diffusivities in a restricted gel. The literature molecular diffusivities were scaled using

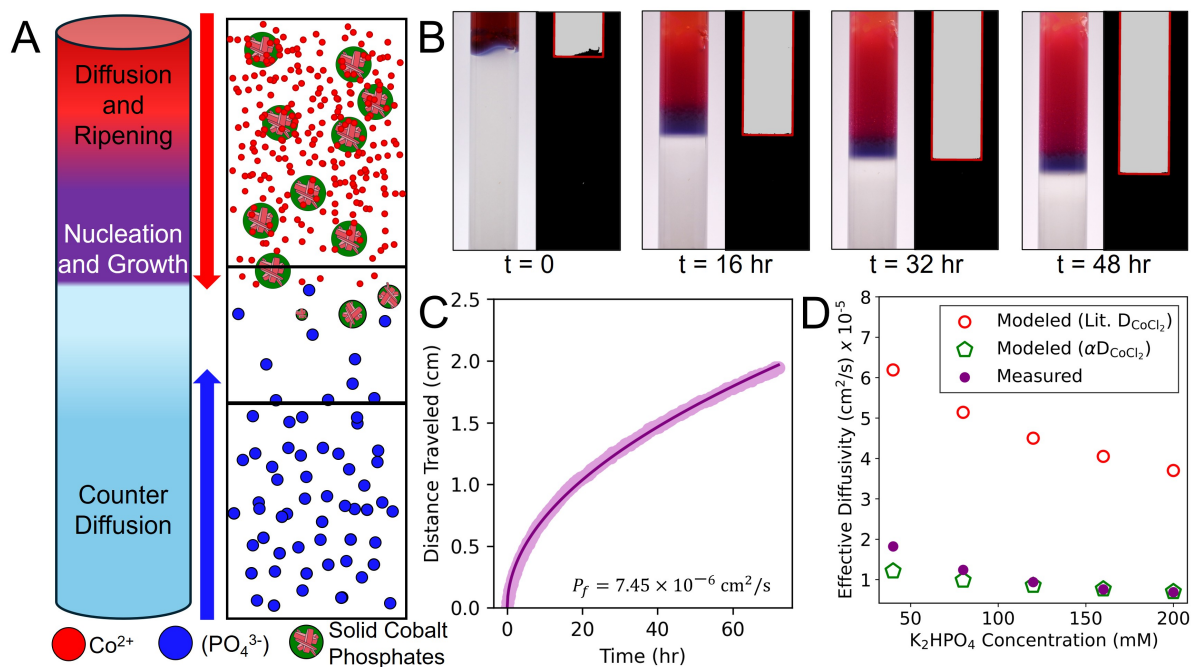


Figure 5.1: A) Graphic of reaction-diffusion coupling between cobalt and phosphate electrolyte solutions in a gel matrix B) Time-lapse images of the reaction-diffusion of 0.5 M CoCl_2 and 0.1 M K_2HPO_4 and the associated mask and parameterized box drawn with object detection. C) Position of the reaction-diffusion front over time, fit with the mean square displacement for 1D Brownian diffusion, $x_f(t) = \sqrt{2P_f t}$, to extract an effective propagation rate, P_f , that characterizes the propagation rate. D) The measured and modeled effective propagation rates (P_f) plotted against increasing concentrations of the counter electrolyte, dibasic potassium phosphate (K_2HPO_4). The red circles are the modeled effective propagation rate coefficients when using literature values of CoCl_2 molecular diffusivity ($D_{\text{CoCl}_2} = 1.086 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$),⁵⁵ $D_{\text{K}_2\text{HPO}_4} = 1.11 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$,⁵⁶ green pentagons are the modeled effective propagation rate coefficients using a pre-factor ($\alpha = 0.186$) applied to both D_{CoCl_2} and $D_{\text{K}_2\text{HPO}_4}$ to match the observed effective propagation rates of the reaction-diffusion front (solid purple).

$\alpha = 0.186$ as a prefactor to approximate the restricted diffusion through the gel.⁵¹ This made the simulated reaction-diffusion system more accurate to the experiment, especially at higher K_2HPO_4 concentrations (Figure 5.1D).

5.3.2 X-ray Scattering for Spatially Dependent Crystallization

Since reaction-diffusion through a hydrogel produces a continuum of dynamic reaction conditions, it must be true that each position in the gel can be treated as discrete with a unique history of supersaturation conditions than can produce various particles.⁵⁷ Due to the large spatial variation in reaction conditions per

sample, and the large parameter space of the reagents, the gel, and the concentrations, X-ray scattering as an *in situ* characterization technique makes it possible to rapidly study crystallization across a large length scale. We performed ultrasmall-, small-, and wide-angle X-ray scattering (USAXS/SAXS/WAXS) at the Advanced Photon Source (APS) at Argonne National Lab to characterize morphology and crystal structure over both time and space in the gels.

The structure of the gels is an important parameter to consider when adding in significant concentrations of an electrolyte for a reaction-diffusion experiment. Gels are dynamic structures and can be prone to structural changes over time as diffusion of the species occurs. Small angle X-ray scattering (SAXS) is a useful technique for determining the structure of the gels. It was found that when adding K_2HPO_4 in concentrations equal to or less than 0.1 M, the structure of the gel was not significantly altered for PEGDA and polyacrylamide. The SAXS data and its analysis for different gel samples with and without ions can be found in appendix A.2.

Figure 5.2 shows the USAXS results for a sample prepared with 5 M CoCl_2 outer electrolyte and a 0.1 M K_2HPO_4 inner electrolyte in a PEGDA (20k Mw, 10 wt%) gel. The sample was allowed to diffuse for approximately 9 hours. Measurements were taken along the length of the gel at the points specified (Figure 5.2A) from the top of the gel to the bottom of propagation front. Standard USAXS at the APS has an effective q range for these samples of 3×10^{-4} to $0.1 \text{ \AA}^{-1}$ (approximately $2 \text{ }\mu\text{m}$ to 6 nm). High-resolution USAXS (HR-USAXS) is able to measure an additional decade into the low q region, 3×10^{-5} to $0.1 \text{ \AA}^{-1}$ (approximately $20 \text{ }\mu\text{m}$ to 6 nm). WAXS, which can measure atomic lattice spacings (q range: 0.8 to $6 \text{ \AA}^{-1}$, 10 to $1 \text{ \AA}$), was also taken for every position.

Using USAXS, the morphologies of the cobalt(II) phosphate precipitates could be identified, which were corroborated in SEM (Figure 5.2B-C). The first precipitate after the featureless gel (Figure 5.2A, 22 mm) that is seen at the propagation front (20 mm) are polydisperse spherical particles (200 nm in diameter). The lack of Bragg peaks in WAXS means they are amorphous (Figure 5.4 and Figure 6.16). From 14 to 18 mm in the gel, the precipitants are monodisperse spheres (410 nm in diameter, PDI of 0.06). These sizes were determined using a sphere fit of the USAXS data rather than the SEM images.⁴⁰ The monodispersity of these particles is surprising, given that typical syntheses of amorphous cobalt(II) phosphate produce highly agglomerated particles that often require a substrate to be synthesized with any regularity.^{58–60} Possible

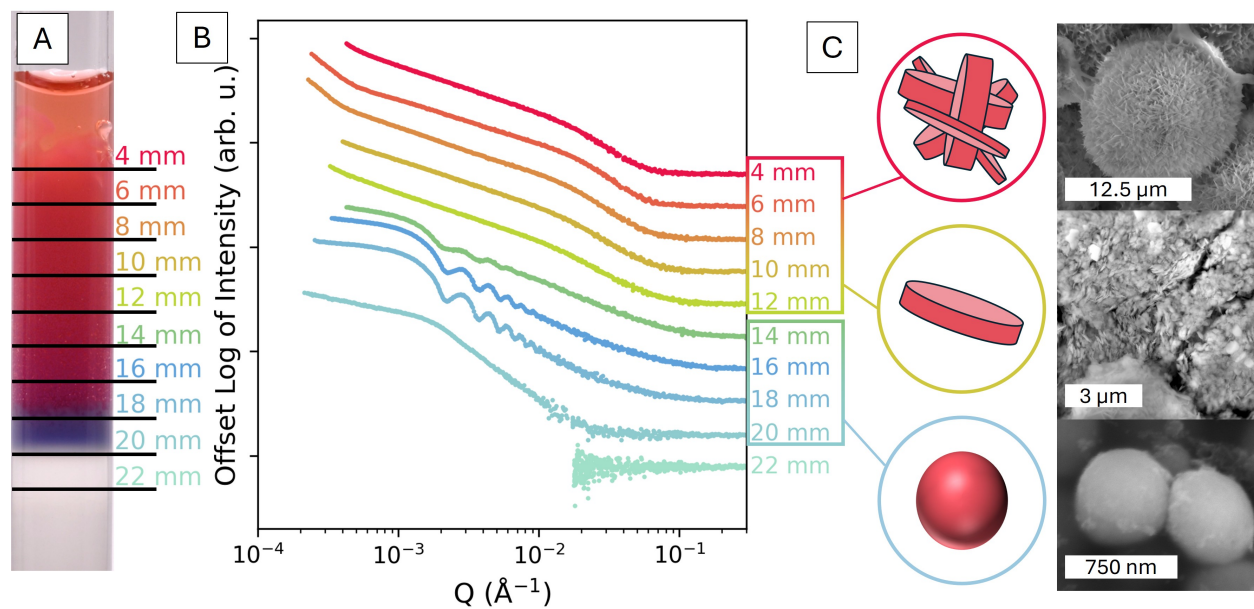


Figure 5.2: **A)** Image of a PEGDA (20k Mw) gel sample prepared in a 4 mm NMR tube with an outer electrolyte of 5 M CoCl₂ and inner electrolyte of 0.1 M K₂HPO₄. Lines are drawn every 2 mm indicating where **B)** Ultrasmall angle X-ray scattering (APS, Argonne) was measured within the gel sample. The curves are grouped by the morphology of the particles present in the sample. The final featureless curve at 22 mm contains no precipitates and is gel only. Plots are offset on the y-axis by a fixed amount from one another. **C)** Morphologies of cobalt(II) phosphate precipitates within the gel identified with SEM imaging of sections of gel, corroborated by the scattering curve.

reasons for this monodispersity will be examined in the discussion.

At 14 mm, the spheres become less monodisperse, and platelets begin to contribute to scattering in the 0.4×10^{-2} to 0.3×10^{-1} q range. SEM was used to identify that platelets formed in the gel above the spheres. This was corroborated in the USAXS data (4 to 12 mm in the gel) by a 'knee' at $q = 2 \times 10^{-2} \text{ Å}^{-1}$ followed by a region with a power-law slope of -2, indicating the thickness of the platelet and a large flat 2D surface. The Guinier-Porod model was used to fit the USAXS data from 4 to 14 mm.⁶¹ The Guinier-Porod model extracts a radius of gyration for the cross-section, R_g , a dimension variable, s , and the Porod exponent. The cross-sectional radius of gyration for the platelets in the 4 to 14 mm region was between 4.0 and 4.3 nm, which corresponds to a plate with a thickness of approximately 14 nm ($R_g = T/\sqrt{12}$). This cross-sectional radius is distinct from the radius of gyration for the total particle, which falls outside the observable q -range and only describes the particle thickness.^{40,62} The dimension variable s is 0 for spheres, 1 for rods, and 2 for lamellae or platelets.⁶¹ The modeled USAXS curve gave an s between 1.7 and 1.9,

indicating a predominantly 2D structure. The Porod exponent in these fits was fixed to 4 since a precipitate should have a sharp interface between itself and the solvent.⁶³ These samples have a higher scattering than expected in the Porod region due to contributions from the gel, which result in lower than reasonable fits for the Porod exponent. For our samples, the R_g and s did not show any systematic trends between the 4 to 14 mm positions.

In SEM, at the top of the gel, larger microparticles could be identified that resembled aggregated platelets. The transport of particles through the gel would not result in typical aggregation, however, but it is not possible to distinguish whether these particles are spheres with decorated platelets or platelets grown dendritically from a central point. The inflection point in the low- q region of the USAXS curve in some of the data (6 and 8 mm) might indicate these larger structures that lie outside the measurable range. The microparticles covered in platelets, the disperse platelets, and the amorphous spheres have all been seen in some shape or form elsewhere in literature,^{64–66} but what is unique about the reaction-diffusion system is that the particles are relatively uniform and lack aggregation since there is no convective or diffusive transport of the large precipitates. This also results in separated particles that are unattached to one another. Reaction-diffusion coupling in hydrogels is a useful strategy for making particles of this kind, which usually require ligands or a surface template to prevent aggregation.⁵⁷

The type of gel that is used as the reaction-diffusion medium has a significant impact on the morphologies that are produced. The reaction of a CoCl_2 outer electrolyte with a K_2HPO_4 inner electrolyte in PEGDA produces the range of morphologies that are seen in Figure 5.2. The concentration of outer electrolyte (between 1 and 5 M CoCl_2) and inner electrolyte (between 0.05 and 0.5 M K_2HPO_4) had little effect, broadly speaking, on which morphologies were present. For instance, similar spheres, platelets, and microparticles were seen regardless of concentration. A polyacrylamide hydrogel prepared as described in the methods section produced largely similar results to the PEGDA gel, with some differences (Figure 5.3A-C). Similar to PEGDA, the polyacrylamide gel produced polydisperse spherical and amorphous particles at the reaction-diffusion front, followed by monodisperse spheres. We can determine the spheres are monodisperse as they exhibit oscillations in the Porod region from the form factor (Figure 5.3C, 16 mm). Unlike with PEGDA, the disperse platelet morphology is not seen. Instead, large crystalline microspheres appear immediately after the amorphous spheres are formed. From SEM (Figure 5.3B), two morphologies can be seen that vary

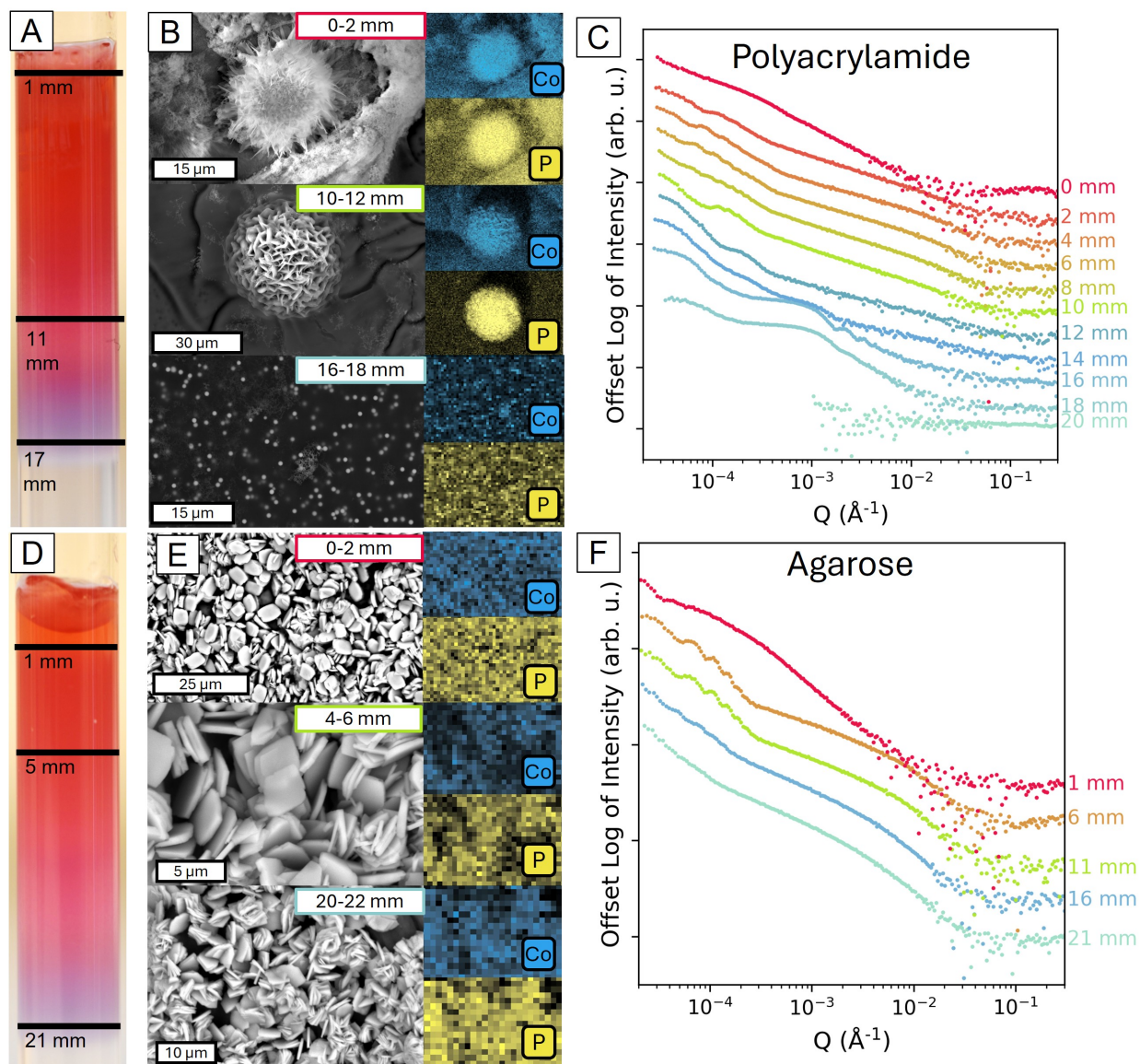


Figure 5.3: A) Photograph of a polyacrylamide reaction-diffusion sample, 5 M CoCl_2 outer electrolyte removed, prepared using 0.1 M K_2HPO_4 inner electrolyte and acrylamide with BisAAm crosslinker (10 wt% T, 5% C). Lines mark the approximate measurement positions in the sample where the B) SEM images and C) HR-USAXS measurements were made. The SEM images were taken on separate but identical samples. In a separate agarose (1 wt%) sample, using identical concentrations of CoCl_2 and K_2HPO_4 , a D) photograph of the sample marks the approximate positions where the E) SEM images and F) HR-USAXS measurements were made. USAXS plots are offset on the y-axis by a fixed amount from one another.

in the surface platelet thickness, with the microspheres at the top of the gel being smaller (approximately 15 μm , from SEM) having wispy thin platelets while the microspheres in the middle of the gel are larger (approximately 30 μm , from SEM) covered in thicker crosshatches of platelets.

The cobalt(II) phosphate that formed in agarose were significantly different compared to the PEGDA and polyacrylamide hydrogels. Throughout the entire agarose gel column, only platelet morphologies were seen. In SEM, the approximate sizes of the platelets could be measured, and at every position the largest dimension of the platelets was between 3 and 5 μm . The thickness of the platelets increased from 300 nm at the propagation front (Figure 5.3E, 20-22 mm) to 1 or 2 μm thick at the top of the gel (Figure 5.3E, 0-2 mm). The platelets at the top also had more square profiles while the propagation front had more leaf-shaped platelets. It is difficult to identify a single attribute of the agarose gel that causes the cobalt(II) phosphates to form platelets instead of spheres. There are many concomitant factors that might contribute to directing the morphology including the weight fraction, the mesh size, and the functional groups which are all significantly different from PEGDA and polyacrylamide. In this work, we've chosen to focus on polyacrylamide since the gel structure is typically more uniform compared to PEGDA,^{67,68} and less prone to rearrangement unlike agarose.^{69,70}

Polyacrylamide also has a more tunable and uniform mesh size range given that the mesh size can be tuned by increasing the ratio of crosslinkers to acrylamide monomers without changing the overall weight fraction of the gel. However, we did not see any significant morphological difference in precipitates between polyacrylamide gels prepared with different crosslinker concentrations or weight fractions (Figure A.1). The results from increasing the weight percent and crosslinking density of the polyacrylamide gels are discussed in appendix A.1.

Pairing HR-USAXS with SAXS/WAXS on reaction-diffusion samples is a very useful tool in following transformations in the precipitates. While USAXS interrogates the shape of the precipitates, SAXS/WAXS makes it possible to determine atomic structure. We can compare the morphology to the crystal structure to gain insights into the crystallization path of the cobalt(II) phosphate (Figure 5.4). With K_2HPO_4 as the inner electrolyte, we can see that the particles begin as amorphous and polydisperse spheres at the propagation front (Figure 5.4A-B, 16 and 18 mm) before becoming crystalline platelets starting at 14 mm. The particles are crystalline from 0 to 14 mm in the gel. The first crystalline peak at 14 mm (Figure 5.4B) are identified by a broad peak at $0.586 \text{ \AA}^{-1}$ ($d = 10.708 \text{ \AA}$) which belongs to a monoclinic phase of cobalt(II) hydrogen phosphate trihydrate ($\text{CoHPO}_4 \cdot 3 \text{ H}_2\text{O}$, PDF 00-039-0702). The intensity of the $\text{CoHPO}_4 \cdot 3 \text{ H}_2\text{O}$ peak decreases moving up the gel column while at the same time two new peaks appear in the SAXS/WAXS

region at 0.8 and 0.95 $\text{\AA}^{-1}$ belonging to orthorhombic cobalt(II) phosphate octahydrate ($\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, PDF 04-009-3836) which increase in intensity moving up the gel column. The monoclinic $\text{CoHPO}_4 \cdot 3\text{H}_2\text{O}$ phase is typically described in literature as a synthetic target,⁷¹ rather than an intermediate in the crystallization of the orthorhombic $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ phase. The crystallization pathway of cobalt(II) phosphate from dibasic potassium phosphate and cobalt(II) chloride is not described in literature. The transition is similar to work by Karafiludis *et al.* who use ammonium phosphates as a precursor, which results in an ammonia-containing struvite phase as well as cobalt(II) phosphate octahydrate.^{65,72}

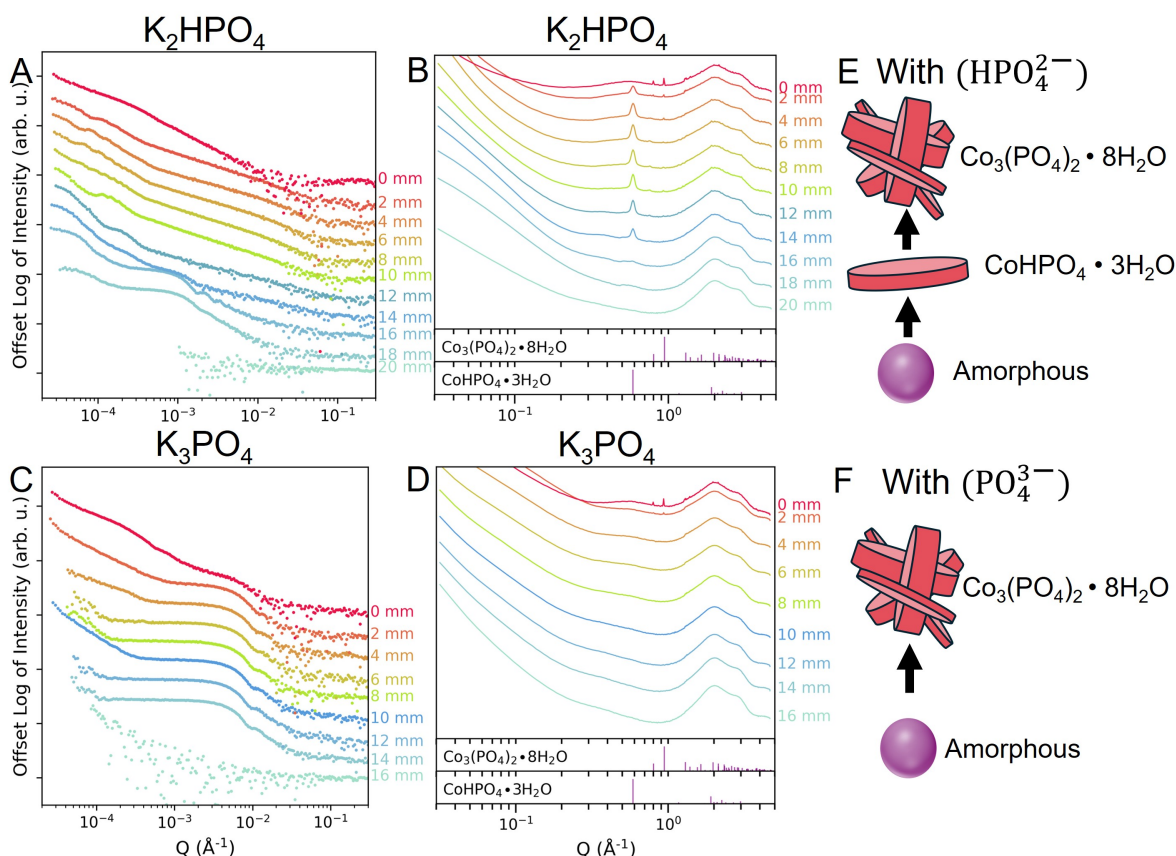


Figure 5.4: A) High resolution ultrasmall angle X-ray scattering (HR-USAXS, APS) of 15 wt% polyacrylamide gels (5% crosslinker) prepared with 0.1 M K_2HPO_4 . and B) merged small and wide-angle X-ray scattering (APS) of the same sample. C) HR-USAXS of 15 wt% polyacrylamide gels (5% crosslinker) prepared with 0.1 M K_3PO_4 and D) merged small and wide-angle X-ray scattering of the same sample. cobalt(II) phosphate octahydrate pattern ($\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, PDF 04-009-3836) and cobalt(II) hydrogen phosphate trihydrate ($\text{CoHPO}_4 \cdot 3\text{H}_2\text{O}$, PDF 00-039-0702) are in purple. E) Morphological transition pathway when using a precipitating agent containing the hydrogen phosphate ion (K_2HPO_4) and F) the pathway when using the phosphate ion (K_3PO_4). USAXS and SAXS/WAXS plots are offset on the y-axis by a fixed amount from one another.

Tribasic potassium phosphate (K_3PO_4) was used as the inner electrolyte in an otherwise identical reaction-diffusion sample with polyacrylamide gel. In USAXS, the K_3PO_4 sample precipitates as spheres throughout most of the gel (Figure 5.4C, 2-16 mm), and the lack of crystalline peaks in the SAXS/WAXS plots suggests that they are amorphous (Figure 5.4D, 2-16 mm). At the very top of the gel (0 mm), however, the Bragg peaks in SAXS/WAXS align with the orthorhombic $\text{Co}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ phase, and the low- q region of the USAXS curve increases in slope along with a 'knee' feature that resembles the same scattering behavior as the sphere-shaped platelet aggregates that are produced from K_2HPO_4 . However, the monoclinic $\text{CoHPO}_4 \cdot 3 \text{H}_2\text{O}$ phase is entirely absent from the SAXS/WAXS curves, and the USAXS plots show a less gradual transition from the amorphous spheres to the orthorhombic microspheres. Since the dibasic potassium phosphate reacts with CoCl_2 as the hydrogen phosphate ion (HPO_4^{2-}), and the tribasic potassium phosphate reacts directly as the phosphate ion (PO_4^{3-}), it is reasonable that CoHPO_4 is only formed when CoCl_2 reacts with K_2HPO_4 . It is also likely that the amorphous $\text{Co}_3(\text{PO}_4)_2 \cdot \text{XH}_2\text{O}$ phase is more stable than the amorphous $\text{CoHPO}_4 \cdot \text{XH}_2\text{O}$ phase since we see the amorphous $\text{Co}_3(\text{PO}_4)_2 \cdot \text{XH}_2\text{O}$ persist in the gel over a longer time and at many positions throughout the gel (Figure 5.4D) compared to amorphous $\text{CoHPO}_4 \cdot \text{XH}_2\text{O}$ which is more transient (Figure 5.4B). This shows a definitive way to direct the crystallization of cobalt(II) phosphate to avoid or travel through the monoclinic $\text{CoHPO}_4 \cdot 3 \text{H}_2\text{O}$ intermediate. Given that pH is a common and useful handle for controlling the crystallization of metal phosphates,^{73,74} this makes it possible to drastically change the crystallization process given that $\text{CoHPO}_4 \cdot 3 \text{H}_2\text{O}$ must expel H^+ to crystallize into $\text{Co}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$.⁶⁵

5.3.3 Crystallization Pathways Examined in Time

We can speculate that the spatial dimension will be similar to the temporal dimension, and that the morphologies that we see throughout the volume of gel at a single snapshot in time will be similar to the evolution of precipitates over time at any given position in the gel. However, this assumption is poor without temporal data. Scattering data from an identical sample to Figure 5.5A was collected in the HR-USAXS (Figure 5.5B) and WAXS (Figure 5.5C) regions over a 12-hour period. Each HR-USAXS measurement took 3 minutes which was followed immediately by a 30 second WAXS measurement. A total of 10 samples were measured simultaneously in this way. The measurements were staggered such that the top of the

gel was measured earlier and the bottom of the gel was measured later, followed by a final measurement at the end of the experiment of every position for every sample. The measurement spacing can be seen best in the background-subtracted WAXS data (Figure 5.5C), while the HR-USAXS data was arranged to illustrate the changes in particle morphology between the measurements (Figure 5.5B).

Using the temporal HR-USAXS data, we can conclude that the mechanism for the crystallization of cobalt(II) phosphate involves dissolution and re-precipitation. The earliest precipitates (light green, light red, and light blue curves) are amorphous spheres, which is the case for every position (1, 6, and 11 mm). The amorphous spheres are larger the further down the gel column they are, which is determined by the shifting of the rounded 'knee' to lower q . This is consistent with classical nucleation theory, as the reagent concentration is lower the further into the gel the reagents diffuse towards each other. The lower concentration results in fewer nuclei, which promotes the growth of larger particles rather than the nucleation of more. We fit the curve below $8 \times 10^{-4} \text{ \AA}^{-1}$ with a simple sphere model until the feature disappeared in some gel positions over time.⁴⁰ Most positions show that the diameter of the spherical precipitates decreases slightly as the larger platelets grow. The spheres in the last position in the gel, 11 mm (Figure 5.5), first increased in diameter before decreasing at the time of the last measurement. This can be seen graphically in Figure A.3. If the reaction had not occurred inside a gel, the growth of the features in lower q might indicate aggregate. However, this behavior is consistent with dissolution and re-precipitation rather than aggregation since the gel prevents the transport of the relatively large precipitates required for aggregation to occur. This is corroborated by SEM images (Figure 5.2C) where particles are seen to be separated without any aggregation.

This general behavior is shared for each of the gel positions in the sample, and all first nucleate as an amorphous sphere. There are some differences between the positions in the gel, which may be accounted for by the different concentration profiles each position experiences. Since the precipitates are larger than the largest measurable dimension in HR-USAXS, and there is a mixture of morphologies, it is not possible to effectively apply a quantitative model. At 6 mm in the gel, we see oscillations in the final scattering profile (Figure 5.5B, 6 mm, dark red), which indicate a more monodisperse dimension or regular structure. This is the same scattering behavior in Figure 5.3F which had platelets of a uniform thickness. It is possible that the features that develop over time in the low- q at 11 mm are also larger spherical structures composed of

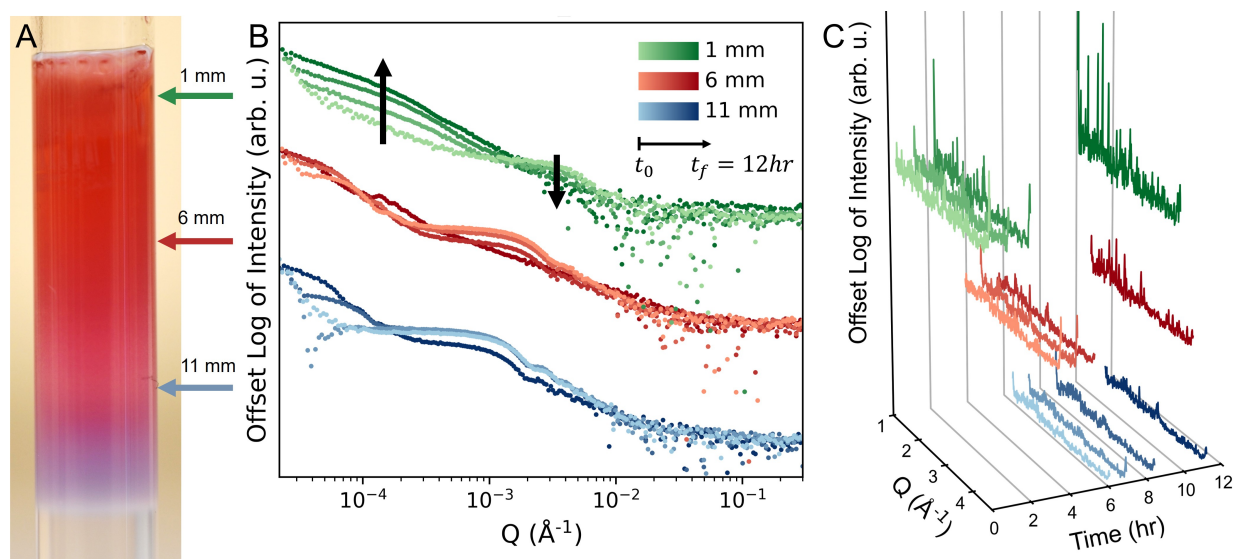


Figure 5.5: **A)** Image of reaction diffusion sample, 5 M CoCl₂ outer electrolyte removed, using 10 wt% polyacrylamide gels (5% crosslinker) prepared with 0.1 M K₂HPO₄. Colored arrows mark the measurement positions in the sample at 1 mm (green, top) 6 mm (red, middle) and 11 mm (blue, bottom). **B)** HR-USAXS (3 min measurement) over a 12-hour period of the same three positions in the sample (1, 6, and 11 mm). Lighter colors are earlier and darker colors are later in experiment window. **C)** WAXS (30 sec measurement) taken immediately after each HR-USAXS measurement. To attempt to follow the reaction-diffusion front, measurements at the three positions were staggered and followed by a final measurement at the end of the experiment. USAXS and WAXS plots are offset from one another on the y-axis a fixed amount depending on the position they were measured at (1, 6, or 11 mm). No additional offsets were applied for measurements made at different times.

smaller uniform platelets. However, the large dimensions of these structures and the overlap with scattering from the smaller spheres at lower q make it challenging to fit accurately. However, the lack of aggregation in SEM and the changes in scattering intensity over time conclusively demonstrate that the crystallization of cobalt(II) phosphate from K₂HPO₄ can proceed *via* dissolution and re-precipitation, which was hypothesized for the cobalt(II) chloride and dibasic ammonium phosphate system.⁶⁵

Additional time-resolved SAXS/WAXS measurements of 20k PEGDA gels were made using the Xenocs Xeuss 3.0 at the University of Washington, which can be seen in Figure A.4 in appendix A.1. It can be seen in this experiment that at the three positions in the gel that were measured (2, 6, and 12 mm from the top of the gel), the same monoclinic CoHPO₄ · 3 H₂O phase was present in different concentrations. Over time, each position in the gel goes through the same crystallization pathway, starting amorphous, then monoclinic CoHPO₄ · 3 H₂O and finally orthorhombic Co₃(PO₄)₂ · 8 H₂O. From the different relative intensities of

the $0.6 \text{ \AA}^{-1}$ peak at the three positions, we can tell the concentration of the monoclinic phase is different depending on where in the gel the crystallization is occurring. This suggests that the crystallization can be controlled by the position in the gel and the unique supersaturation environment at each distinct position.

5.4 Discussion

It is important that the results from this work be understood in the context of the larger field of studying crystallization *in situ*. Often, crystallization in a liquid solution is studied *via* a liquid or flow cell using transmittive techniques like TEM, X-ray scattering, and X-ray or UV-Vis spectroscopies.^{21,75} These techniques are typically time intensive, requiring significant effort to investigate different reaction conditions. This makes many systems inaccessible for study due to the large parameter space of each reagent. Accelerated exploration methods, such as lab automation with liquid handling robotics,^{18,76} are superior for sampling the wider phase space, but are typically challenged at investigating products *in situ*. Probing reaction-diffusion coupling in hydrogels with X-ray scattering techniques combines the scale of automated high-throughput investigation with the temporal and wide length scales achievable with traditional methods.

X-ray scattering exposes unique crystallization behavior in reaction-diffusion

An interesting consequence of performing the precipitation of cobalt(II) phosphate in a gel, which would not have necessarily been apparent to any other analytical technique, was the appearance of monodisperse, amorphous, spherical particles. For every sample, at every position in the gel, the first precipitates that formed were amorphous spherical particles with varying levels of monodispersity. This can be seen in Figure 5.6 where each gel sample first precipitated spheres, which dissolved at the expense of larger platelet structures. It is possible that the reason for this monodispersity is because of the incredibly low K_{sp} of the cobalt(II) phosphate species, which results in there effectively being burst nucleation at every point in the gel as the CoCl_2 diffuses. If the K_{sp} were higher, then monodisperse particles would only be found at the very top of the gel, until they dissolved and re-precipitated as platelets, where the concentrations were highest. It is possible then, that the bottom of the gel would experience periodic precipitation where the concentration would initially be too low for nucleation, but after enough time, the diffusing CoCl_2 would increase the cobalt concentration until nucleation and subsequent growth were to occur.

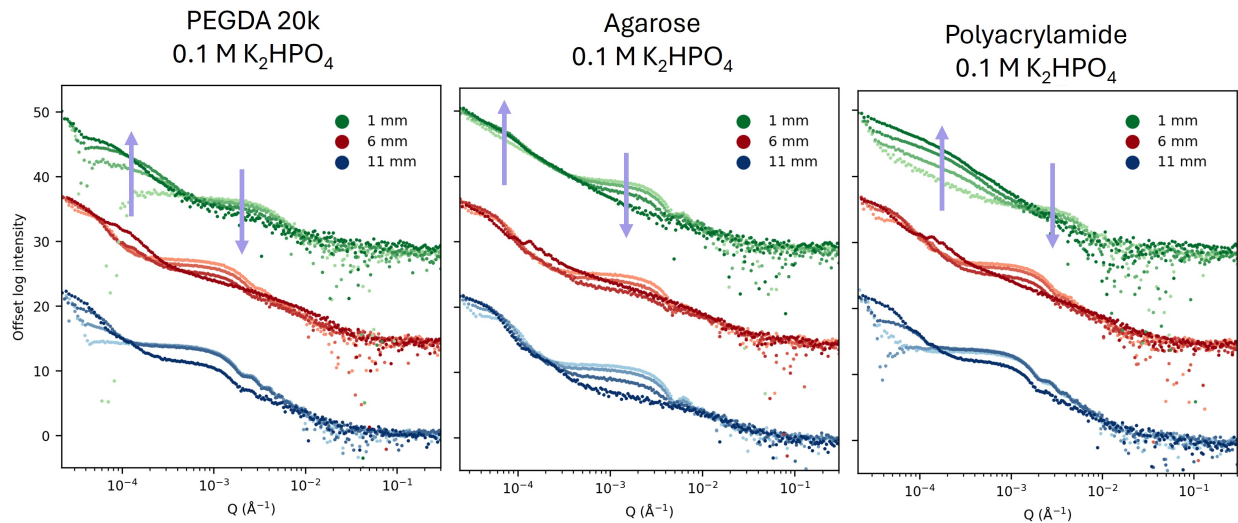


Figure 5.6: USAXS of reaction-diffusion samples, each with a 5 M CoCl_2 outer electrolyte and the same 0.1 M K_2HPO_4 inner electrolyte. Each sample was prepared in a different gel: 20k PEGDA (10 wt%), agarose (1 wt%), and polyacrylamide (10 wt%T, 5% C). Each gel is identified in the title of each plot. Samples were allowed to react over 12 hours. The lightest-colored curves were measured first, while the darkest colored were measured last. USAXS and WAXS plots are offset from one another on the y-axis a fixed amount depending on the position they were measured at (1, 6, or 11 mm). No additional offsets were applied for measurements made at different times.

It was immediately apparent through scattering and SEM imaging that precipitation in the agarose produced a different morphology than the PEGDA and polyacrylamide samples (Figure 5.3). The agarose produced thick platelets throughout the entire volume of gel. The platelets at the front of the propagation curve were monoclinic $\text{CoHPO}_4 \cdot 3 \text{H}_2\text{O}$, much like the PEGDA and polyacrylamide samples, and the final platelets were orthorhombic $\text{Co}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$, as can be seen in Figure 5.7. So while the atomic structure followed a similar trend to the PEGDA and polyacrylamide samples (Figure 5.7), the platelets never turned into microspheres like in PEGDA and polyacrylamide. No amorphous phase was measured, suggesting that any amorphous particles are shorter-lived or not present in the agarose gel. Given that PEGDA, polyacrylamide, and agarose all have very different functional groups and mesh sizes, the differences in behavior are possibly due to the free volume, or the size of the largest pores on the micrometer scale. Agarose was prepared at 1 wt% compared to the 10 wt% of polyacrylamide and PEGDA, which would make these pores much larger. Under confined conditions in diffusion regimes, it is established that the stability of prenucleation clusters are affected by local compositional changes.⁷⁷ In the confined hydrogel environment, these

species are more long-lived.⁷⁸ The larger pores in agarose could change the number and stability of available prenucleation clusters so that precipitation proceeds closer to bulk conditions.^{79,80}

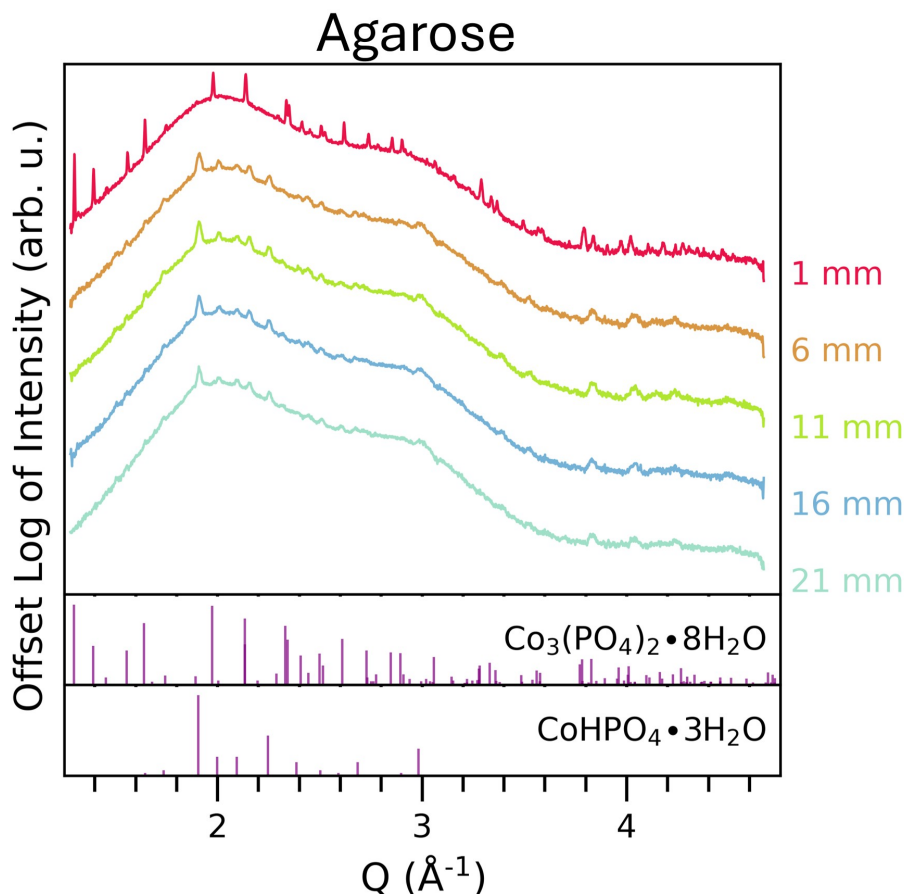


Figure 5.7: Reaction-diffusion sample prepared 1 wt% agarose and a 5 M CoCl_2 outer electrolyte with a 0.1 M K_2HPO_4 inner electrolyte. WAXS was taken at the same time as HR-USAXS in Figure 5.3F. WAXS measurements were offset on the y-axis a fixed amount from one another.

By observing the thickness of the blue/purple reaction-diffusion front, it is also apparent that while the spatial and time dimensions are similar, they do not provide a one-to-one analog of each other regarding the reaction conditions. For reaction-diffusion samples that use K_2HPO_4 as the inner electrolyte, there is a sharp transition between the blue/purple reaction-diffusion front and the rest of the red/pink precipitation products. This blue/purple band is always ~ 2 mm in thickness and only transitions to red/pink as the band travels down the gel column. This results in an interesting phenomenon where, after a significant amount of time, on the order of days or weeks, the band will remain in place. These colors are often

attributed to the hydration state of the cobalt(II) phosphate, with less hydrated species tending towards more violet colors. Cobalt phosphates have been used as pink and purple pigments since antiquity. Anhydrous cobalt(II) phosphate is described as violet, the tetrahydrate as typically violet/pink, and the octahydrate as fully pink.⁸¹ It is expected that the level of hydration is a function of time in an aqueous environment, which would mean that the violet band would shrink over time as the diffusion progressed. However, this is not observed (Figure 5.1). The band thickness remains relatively unchanged even after many weeks. This suggests that the hydration, like the morphology, is a product of the relative and absolute concentrations of the reactants. When the ions in the outer electrolyte are depleted and the reaction-diffusion front stops or slows considerably, the conditions throughout the gel are effectively frozen with less growth and nucleation possible. This maintains the band's color and size. Over longer time scales, however, on the order of many months, the band will eventually fade, and the smallest particles will experience Ostwald ripening. This regime requires more investigation as samples need to be undisturbed for 4–8 months at a time.

The dynamic nature of these systems over longer timescales introduces additional complexities beyond what is explainable by classical nucleation theory. In specific instances when K_3PO_4 was used as an inner electrolyte, samples that were left for multiple weeks with the outer electrolyte removed developed chaotic banding throughout the gel column (Figure 5.8). This was seen regardless of the gel used, and only for the reaction between $CoCl_2$ and K_3PO_4 . The position and thickness of the bands depended on the hydrogel with polyacrylamide, PEGDA, and agarose, producing noticeably different band morphologies for each. The selected polyacrylamide sample had a small number of faint bands with less defined edges, while the two selected PEGDA samples had numerous dark, well-defined bands. The selected agarose sample had a larger number of thicker bands. Differences such as these are common in Liesegang systems as the gel is a source of impurities that affect emergent properties like macro scale organization.⁸² When driven by periodic precipitation, the band structure is typically more ordered, while on longer time scales Ostwald ripening creates more chaotic band structures in post-nucleation coarsening as emerging concentrated regions of particles compete with one another.^{31,83} Given the length of time required for the banding to develop, coarsening is the most likely mechanism for the bands in Figure 5.8.

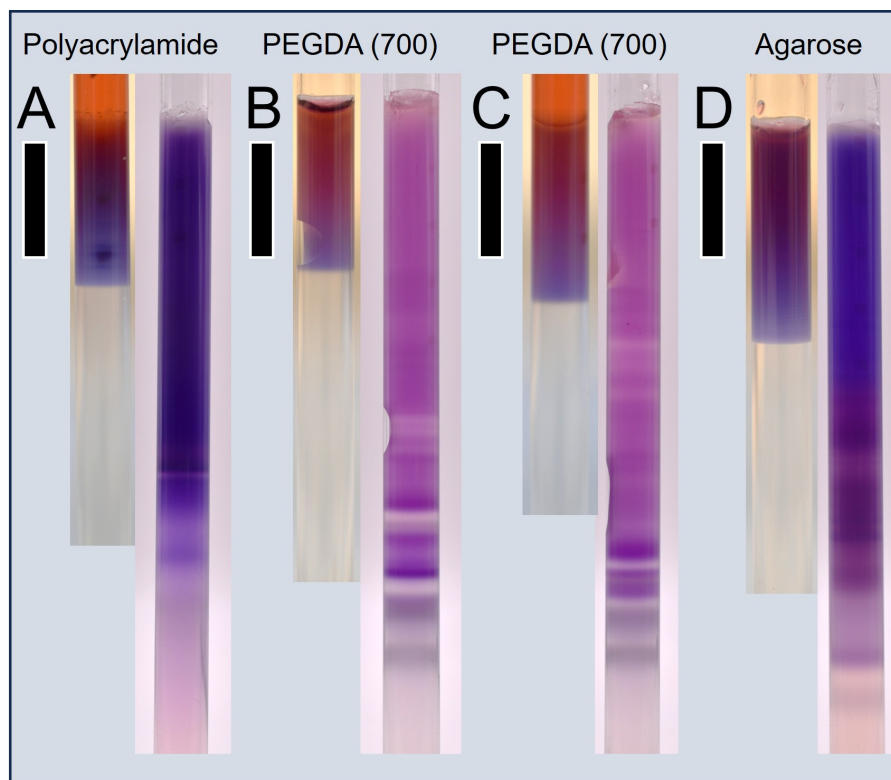


Figure 5.8: Photos of reaction-diffusion samples with a 5 M CoCl_2 outer electrolyte and a 0.1 M K_3PO_4 inner electrolyte 12 hours (left) and 26 days (right) after adding starting the reaction-diffusion experiment in a **A**) polyacrylamide gel (10 wt%T, 5%C), **B,C**) 700 Mw PEGDA, and **D**) 1 wt% agarose. Black scale bars are 10 mm.

5.4.1 Future Directions

Reaction-diffusion coupling in hydrogels has been shown to be a potentially useful methodology for efficiently investigating a wide range of reaction conditions. However, there are significant drawbacks that keep it from being a more generally useful tool. First, careful modeling and analyses of scattering data rely on a known concentration to make inferences on an absolute scale. Even though it is possible to know the total mass of the reagents added to the inner and outer electrolytes, the concentration gradient produced by the reaction-diffusion coupling makes it challenging to know the exact concentration at every point even though the total mass might be known. Accurate concentration data would make it possible to measure volume fractions of the various morphologies over time and even extract kinetic parameters of the crystallization. Achieving this would be a significant improvement over the current measurement strategies for crystal evolution, which are typically not parallelizable like a self-contained hydrogel sample is. A robust simulation

strategy coupled with accurate concentration measurements is required to meet this goal. This would require tuning the reaction-diffusion model (specifically the reaction rates and diffusion rates) against ICP or absorbance measurements to effectively create a 'digital twin'.

This approach is gaining traction in closely related fields. Ritchhart *et al.* model the Liesegang phenomena specifically using a machine learning method to predict and describe the position of bands and effective rate of diffusion of the propagation front.⁸⁴ With the simple modeling that was performed so far in this study (Figure 5.1), the accuracy of the model could not be confirmed as the modeled concentration was never matched to measured values with a technique like ICP. A first initial step for this work would be first establishing the accuracy, or lack thereof, for this numerically solved PDE model for a number of the reaction-diffusion samples and then tuning it to produce accurate results. The power of the model would not be necessarily in the accuracy of the individual parameters, such as the molecular diffusivities or reaction rates, but in the ability to accurately account for concentration to couple with a scattering technique. This would also make it possible to extend this methodology to other systems with similarly complicated parameter spaces like calcium carbonates. This material system experiences strong pH and concentration-dependent morphologies and structures that are well understood individually,⁸⁵ but combining multiple parameters together requires accelerated methods.¹⁸ It might even be possible to create sample holders with multiple outer electrolytes to produce a larger number of conditions per sample.

Improving the accuracy of these models would enable an additional area of study, which is decoupling the product of the precipitation from the reaction-diffusion coupling. The goal is to produce the same or similar morphologies that were produced in the hydrogel, but using more directly scalable methods like plug-flow reactors (PFRs) and constantly stirred tanks (CSTRs). Reaction-diffusion in gels has demonstrated attractive synthetic,^{27,28,86–88} and separative capabilities,^{37,89,90} but reaction-diffusion in gels is challenging to scale. This is because the precipitation process is prohibitively slow for commercial applications, not to mention that the precipitates are difficult to separate from the gel once the 3D network fixes them in place. It is desirable to replicate the product using a bulk mixing method, which would allow the solid product to be free to transport away from the reaction site. We hypothesize that the inherent uniqueness of the reaction-diffusion system is in the concentration history over time. If the concentration over time can be replicated inside a bulk mixing reactor, then it may produce the same products. We have begun preliminary experi-

ments towards this end by adjusting the concentration of a sample to follow a simple concentration profile over time. We hypothesize that this experiment will separate the effects of the gel from the concentration history created by the diffusion regime. Our gel results strongly suggest that the identity of the inner electrolyte, between K_2HPO_4 and K_3PO_4 , is more important than the functional groups of the gel in directing the crystallization. Changing the concentration precisely of a bulk mixing reaction to match a position within the gel would therefore produce similar morphologies. Given that the cobalt(II) phosphate crystallization is mediated by a dissolution and re-precipitation, it may be preferable to use a different material system. The overarching goal would be to leverage the high throughput and efficient measurements in hydrogels for transferal to scalable reactor systems that would enable synthesis and separation commercially.

5.5 Conclusion

Using USAXS/SAXS/WAXS combined with SEM, we can quickly and efficiently study a host of morphologies present in the cobalt(II) phosphate reaction-diffusion system in hydrogels. We identify how changes in the environment can affect the precipitation behavior of the solutions inside various representative hydrogels. We investigate the effect of reagent concentration and identity (K_2HPO_4 , K_3PO_4) in addition to gel weight fraction and type (PEGDA, agarose, and polyacrylamide). We find the reaction-diffusion in hydrogels to result in disaggregated and uniform particles, producing a large library of morphologies that were efficiently identified. Performing the reaction in a gel made it possible to take temporal measurements at various positions, which proved that the crystallization of cobalt(II) phosphate proceeds *via* dissolution and re-precipitation of amorphous species that had previously been hypothesized in similar systems.²³ We find X-ray scattering in hydrogels to be an effective method for efficiently characterizing structure during crystallization. We envision this method as extendable to other precipitation systems both in and out of hydrogels.

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Chapter 6

Separative Crystallizations in Hydrogels Studied with X-ray Scattering

6.1 Chapter Introduction

Hydrometallurgical reactions form a complicated web of interdependencies with respect to the chemistry of the reagents, their concentration, and non-participating additives which affect crystal growth.^{1,2} This results in an extremely large parameter space under even the most well-behaved single reaction systems.^{3,4} The introduction of multiple species, with competing reaction events, further compounds this problem as cooperative effects between the reagents in a system are commonplace.⁵ In synthesis, whether it is industrial or lab-scale, it is assumed that the process will have a carefully controlled feedstock composition. This assumption is often taken for granted as in the industrial separations space, very few guarantees are made with respect to the composition of the feedstock. Separation sciences must concern itself with every competing side reaction, non-equilibrium growth, and cooperative effects between every constituent of an ambiguous feedstock. Capturing this requires accelerating our in-lab investigations to more efficiently understand the parameter space. In many cases, the added perspective that a comprehensive study gives us can reveal local minima within the landscape that are exploitable for separations.⁶

Feedstocks containing cobalt and nickel are an example of an industrially relevant system. Cobalt and nickel are important materials in battery chemistry as well as alloys.^{7,8} The challenge with cobalt and nickel

specifically is that, when mixed together, as they often are both in nature as well as industry,^{9,10} they are extremely challenging to separate due to their similar properties.^{11,12} Precipitation of mixed feedstocks of cobalt(II) and nickel(II) have also been shown to behave significantly differently compared to each individual ion.¹³ In chapter 5, we demonstrated the ability of X-ray scattering paired with electron microscopy to efficiently explore large portions of the crystallization parameter space with respect to structure and morphology in reaction-diffusion coupled systems. In this work, we demonstrate that reaction-diffusion coupling can help shine a light on the behavior of mixed feedstocks. We use a mixed feedstock of cobalt(II) and nickel(II) to demonstrate this, in addition to the pure cobalt(II) and pure nickel(II) feedstocks which are required comparisons. This work was done in collaboration with Joelle V. Scott, Abdul Moez, Elias Nakouzi, David S. Bergsman, and Lilo D. Pozzo.

6.2 Experimental

6.2.1 Materials

All chemicals were used as received. Cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; reagent grade), nickel(II) chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; EMSURE $\geq 98\%$) dibasic potassium phosphate (K_2HPO_4 ; $\geq 98\%$), and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP; $\geq 95\%$) were purchased from Sigma-Aldrich. Poly(ethylene glycol) diacrylate (PEGDA; 500, 700, 4k, and 20k g/mol) was purchased from Polysciences (Warrington, PA), potassium carbonate (K_2CO_3 ; $\geq 99\%$) was purchased from VWR, and sodium hydroxide (NaOH ; $\geq 97\%$) was purchased from Fisher Scientific.

6.2.2 Sample Preparation

Gels were prepared identically to those in chapter 5. However, the gels used in this chapter were exclusively poly(ethylene glycol) diacrylate (PEGDA) at 10 wt% of the total solution mass. PEGDA gels were used in three molecular weights; 575 g/mol, 700 g/mol, 4,000 g/mol, and 20,000 g/mol. Each had a subsequently longer ethylene glycol backbone. PEGDA gels were prepared as aqueous solutions with 0.15 wt% of lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP), based on the total mass of the sample, as the photoinitiator to generate free radicals for polymerization. Each gel was prepared in a brown dram vial by

mixing aqueous stock solutions of either PEGDA with photoinitiator, counter ion (if necessary), and additional water to achieve the desired weight fraction. The counter ions were prepared at the desired molarity with respect to the mass of water, not the mass of the total solution which included the mass of polymer. After all solutions were added to the vial in a dark room, the solutions were vortexed and allowed to stand undisturbed until any bubbles had dissipated. The solutions were then dispensed into a 4 inch (103.5 mm) Wilmad-LabGlass™ thin walled high-throughput NMR tube, 5 mm OD (Fisher Scientific), using a long glass pipette and rubber bulb. This was done carefully to avoid bubbles and gel on the walls of the tube above the gel line. The NMR tubes were chosen for their regularity in thickness between tubes to aid sample-to-sample comparisons in scattering data.

At the beginning of the reaction-diffusion experiment, a small amount of concentrated feedstock was placed on top of the gel. The feedstock was 100 μL in volume and contained either 5 M CoCl_2 , 5 M NiCl_2 , or a 5 M mixture of $\text{CoCl}_2\text{:NiCl}_2$ (1:1). The sample was allowed to diffuse and react for at least 8 hours.

6.2.3 X-ray Scattering Measurements

X-ray scattering measurements were made identically to those in chapter 5. ultrasmall-, small-, and wide-angle X-ray scattering (USAXS) experiments of reaction-diffusion samples were performed using the USAXS instrument at Advanced Photon Source, Argonne National Laboratory, beamline 12-ID-E.^{14,15} The combined q range was between 1×10^{-4} to $0.3 \text{ \AA}^{-1}$ for USAXS (3×10^{-5} to $0.3 \text{ \AA}^{-1}$ for high-resolution USAXS), 0.03 to $1.3 \text{ \AA}^{-1}$ for SAXS, and 0.8 to $6 \text{ \AA}^{-1}$ for WAXS; here $q = 4\pi \sin(\theta)/\lambda$, where λ is the wavelength and θ is one half of the scattering angle. The X-ray energy for standard USAXS/SAXS/WAXS was 21 keV ($\lambda = 0.5904 \text{ \AA}$). X-ray photon flux was approximately $5 \times 10^{12} \text{ mm}^{-2}\text{s}^{-1}$ in standard USAXS operation and $1 \times 10^{12} \text{ mm}^{-2}\text{s}^{-1}$ in high-resolution USAXS. Combined USAXS/WAXS measurements had a time resolution of 3.5 min per run. Samples consisted of hydrogels between 1 and 20 wt% in 5 mm OD Wilmad-LabGlass high throughput NMR tubes (Fisher Scientific) held in place by an ad hoc PLA printed holder.

Hydrogel samples were prepared for SAXS/WAXS at the University of Washington by preparing the gel in the same manner as described previously, but transferred into a resin printed cartridge stage with 1 mm Kapton (polyimide) film walls in the beam path and photopolymerized using a UV lamp (365 nm).

SAXS/WAXS was performed on a Xenocs Xeuss 3.0 (Grenoble, France) powered by microfocus GeniX 3D X-ray generator for Cu K α (1.5406 Å⁻¹ wavelength, 8.05 keV) and a Dectris EIGER 2 1M X-ray detector. The measurements were made at detector distances of 1.80 m, 0.90 m, 0.37 m and 0.05 m. The 2D images were reduced and merged using XSACT 2.10 from Xenocs (Grenoble, France).

6.2.4 SEM Imaging

SEM images were made identically to those in chapter 5. Scanning microscopy images and energy dispersive spectroscopy elemental maps of samples were taken using a Thermo Fisher Scientific Phenom Pharos G2 SEM-STEM desktop instrument. Reaction-diffusion gel samples were prepared by extracting and dissecting the gel while still hydrated into 2 mm thick cross sections. The polyacrylamide and agarose gel samples were soaked in ethanol to remove the metal chloride solution and desiccate the gel samples before drying under low vacuum at room temperature. PEGDA gel samples were soaked in water to remove chloride salts and desiccated in a vacuum oven. The dried gel cross sections were fixed to a standard aluminum pin stubs using double sided carbon tape with aluminum base and 5 mm width (Electron Microscopy Sciences; Hatfield, PA).

6.2.5 Diffusion Measurements

Diffusion measurements were made identically to those in chapter 5. Using a Nikon D5600 camera body with a Nikon AF-S DX Micro Nikkor 40 mm (f/2.8G) lens and intervalometer, images of samples were taken every 5 minutes after the addition of the outer electrolyte to the top of the gel. A ring light and white background were used to image the samples. The samples were held upright by a printed PLA stand, and were covered using the provided plastic cap. Using the OpenCV Python package, each frame of the video had the color of the precipitant isolated using a hue, saturation, and value (HSV) mask. A contour was drawn around the masked area using a parameterized box of least area. The width of the box, converted to centimeters, was extracted from every frame of the timelapse.

6.3 Results

To characterize the morphology of precipitates with statistical relevance, scattering measurements are the preferred technique compared to imaging, which assesses only a snapshot of a small number of particles. In these hydrogel systems, particles are often large, on the order of hundreds of nanometers, even a few microns. X-ray scattering at ultrasmall angles (USAXS) is therefore required. As previously discussed in subsection 3, these measurements take an incredibly long time when using a lab-scale instrument. This makes particle accelerators extremely attractive for this system, as they can reduce measurement times from hours to seconds. Previously, X-ray scattering in combination with SEM helped in analyzing the crystallization of cobalt(II) phosphate from CoCl_2 and K_2HPO_4 in chapter 5.

A discussion of the different backgrounds is required before understanding the samples. Every sample in this chapter was prepared with PEGDA. Figure A.5A includes USAXS measurements of the PEGDA gels used in this experiment. These plots are best used as a comparison to the following PEGDA USAXS data and not as direct measurements of the structure of the gel. This is because a Bonse-Hart configuration for USAXS has a much higher background in the region of interest for the gel structure. Given the already low scattering for the gels compared to the quartz sample container, the SAXS measurements taken in Figure A.12–A.16 are more relevant to the structure. In USAXS, however, the 575 and 700 g/mol PEGDAs have a significant amount of scattering compared to the longer PEGDAs, 4k and 20k, which is indicative of features in the USAXS size range. These features are 40 to 70 nm in size and are heterogeneities within the gel. The same voids are absent in the longer 4k and 20k PEGDAs as the longer ethylene glycol polymer backbone creates a more homogenous structure.¹⁶ More thorough discussion of this, along with USAXS scattering measurements of PEGDA gels prepared with the various cations, can be found in Figure A.5, appendix A.1.

6.3.1 Crystallization of Co/Ni with NaOH and K_2CO_3

Sodium Hydroxide

Beginning with the samples prepared with NaOH, the majority of samples did not fully gel. Higher molecular weights combined with higher concentrations of NaOH were detrimental to the formation of the 3D

network. One of the reaction-diffusion samples that did gel was samples with 0.05 M and 0.1 M NaOH in 700 molecular weight PEGDA. The 0.05 M NaOH had poorer scattering above the background due to the low concentration of precipitates. This can be seen in Figure A.6. A concentration of 0.1 M NaOH in 700 molecular weight PEGDA was the highest counter ion concentration that allowed gelation (Figure 6.1).

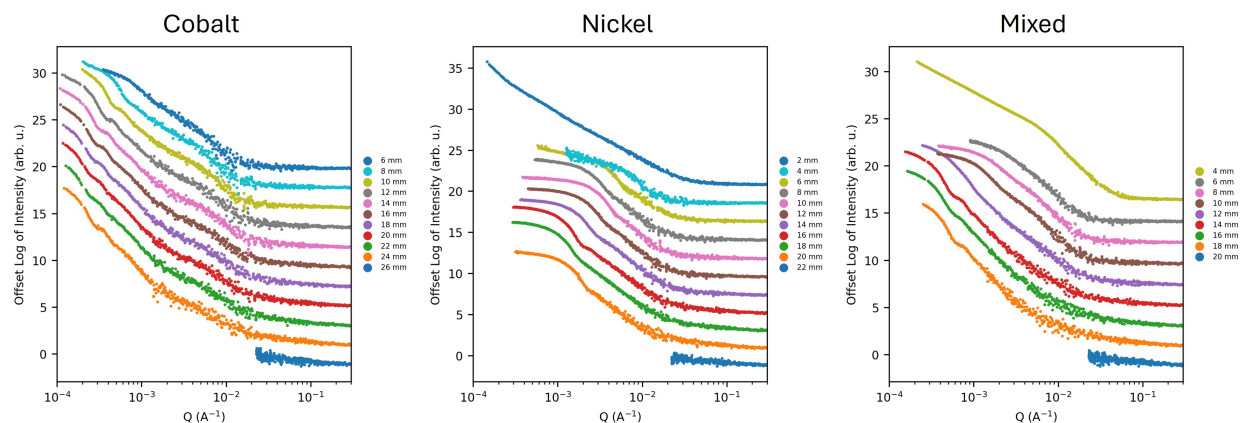


Figure 6.1: USAXS curves of 700 molecular weight PEGDA gels prepared with 0.1 M NaOH with outer electrolytes of 5 M CoCl_2 , NiCl_2 , and a 1:1 Ni:Co mix. Measurements were taken from the meniscus of the outer electrolyte (0 mm) to below the bottom of the reaction-diffusion front where outer electrolyte ions had yet to diffuse to. USAXS measurements were offset on the y-axis a fixed amount from one another.

When using a cobalt(II) chloride outer electrolyte, the cobalt(II) hydroxide particles that form are large and monodisperse spheres. These spheres are almost beyond the resolvable q -range and are approximately 3 to 6 μm in radius, though fitting with confidence is difficult without seeing more of the Guinier region. The largest spheres are at the bottom of the gel, while the smallest are towards the top. When using a nickel outer electrolyte with a 0.1 M concentration of NaOH (Figure 6.1) the particles are spheres, similar to cobalt, with the largest at the bottom of the diffusion front. The nickel(II) hydroxide particles are significantly smaller than cobalt(II) hydroxide precipitates, which might suggest that they nucleated more quickly. In the mixed outer electrolyte then, where NiCl_2 and CoCl_2 are in a 1:1 ratio, we see that after the initially large leaf-shaped platelets form, a curve resembling the smaller nickel spheres develops at 6 mm. Between 10 and 12 mm, the scattering profile transitions to a shape most closely resembling the cobalt particles. These persist until the end of the diffusion front until the precipitate is no longer present at 20 mm. No intermediary state is discernible. While USAXS does not provide a chemical analysis, it is with confidence that we say that the morphologies of the particles undergo a transition. This could be evidence of a separation between

cobalt and nickel species midway through the volume of the gel. This strongly points towards NaOH being a candidate for further elemental analyses such as SEM-EDS, ICP, or XAS.

Potassium Carbonate

Gels prepared with above 0.1 M K_2CO_3 also disrupted the gelation of PEGDA making it unable to hold its shape. Higher PEGDA molecular weights were less likely to gel properly when adding K_2CO_3 , while lower molecular weights were more likely. Of the samples that gelled, 700 and 4k molecular weight PEGDA with two counter ion concentrations, 0.05 and 0.1 M, were measured. Appendix A.1, Figures A.7–A.9 include the 0.05 M and 700k PEGDA measurements, while Figure 6.2 shows the scattering of 0.1 M K_2CO_3 in 4k PEGDA as a representative system.

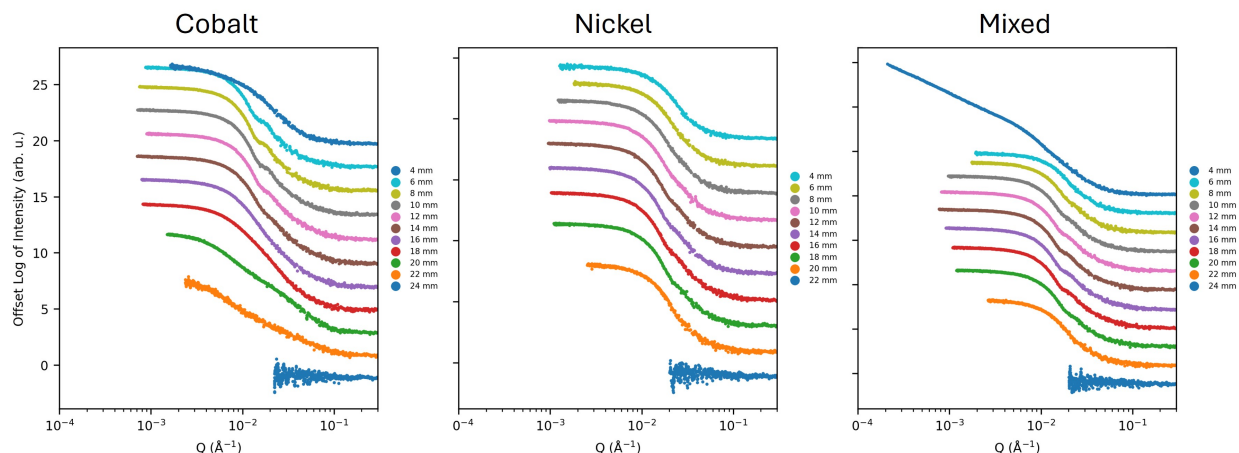


Figure 6.2: USAXS curves of 4k molecular weight PEGDA gels prepared with 0.1 M K_2CO_3 with outer electrolytes of 5 M $CoCl_2$, $NiCl_2$, and a 1:1 Ni:Co mix. Measurements were taken from the meniscus of the outer electrolyte (0 mm) to below the bottom of the reaction-diffusion front where outer electrolyte ions had yet to diffuse to. USAXS measurements were offset on the y-axis a fixed amount from one another.

At the top of the 4k PEGDA containing K_2CO_3 and a $CoCl_2$ outer electrolyte, the scattering profile shows oscillations in the Porod region that indicate monodispersity (Figure 6.2). In the cobalt outer electrolyte sample specifically, the particles are monodisperse at the top of the gel, and polydisperse towards the bottom. This behavior is similar to the crystallization behavior of cobalt(II) phosphate seen in chapter 5, where polydisperse particles nucleate first and then grow more monodisperse. This behavior is flipped for the nickel and mixed outer electrolyte samples (Figure 6.2), which may indicate a difference in reaction

kinetics. Classical nucleation mechanics would predict the smallest monodisperse particles eventually growing into larger polydisperse particles, which is not true for the cobalt sample. However, the nucleation at the top of the gel is occurring where the 5 M outer electrolyte and the 0.1 M counter ion meet, likely resulting in a burst of nucleation, creating many similarly sized precipitates. So the monodispersity of the particles at the top of the gel does in fact follow more classical mechanics. Towards the bottom, the concentrations of the reagents are low, resulting in nucleations that are more spread out in time.

6.3.2 Crystallization of Co/Ni with K_2HPO_4

The final counter ion used in reaction-diffusion experiments was dibasic potassium phosphate. As was also presented previously, the morphology of the particles changes significantly throughout the volume of the gel. In general, the $CoHPO_4$ species precipitated first as amorphous spheres then crystallized into platelets. The $NiHPO_4$ precipitated as amorphous spheres only, and the mixed outer electrolyte samples closely resembled the $NiHPO_4$ spheres in size, shape, and amorphous structure. There is no major difference between the different molecular weights of PEGDA and the size and morphology of the precipitates for K_2HPO_4 . The precipitates were all large (300 nm to 3 μ m or more) relative to the NaOH and K_2CO_3 particles. The cobalt precipitates were the largest, with many particles growing to hundreds of microns so that individual particles could be distinguished by the naked eye. Figure 6.3 are USAXS curves along the length of the entire sample for every combination of the three outer electrolytes ($CoCl_2$, $NiCl_2$, and 1:1 mix) for each concentration of K_2HPO_4 (0.05, 0.1, and 0.5 M), and for every molecular weight of PEGDA (575, 700, 4k, and 20k g/mol). There was no significant difference between the scattering of the samples with respect to the molecular weight of PEGDA. The only significant difference was the scattering of the gel background. The 20k PEGDA will be used to represent the results (Figure 6.3). A discussion of where they deviate will follow.

Cobalt Feedstock

For the three concentrations of K_2HPO_4 with a cobalt outer electrolyte (20k PEGDA) in Figure 6.3, the very top of each sample has large platelet structures that can be attributed to large microspheres with surface platelet growth (Figure 6.4A). The size of the spherical cobalt(II) phosphate precipitates increases as the

concentration increases, which is expected given that there are simply more monomers in solution. From SEM images (Figure 6.3), we can tell that the particles are uniformly all around $10\ \mu\text{m}$ in size, which is far outside the USAXS range. The individual particles are dendritic in nature, as the particles are all made up of small platelets (Figure 6.3C). Since no dispersed platelets are present, it is more likely that these are not aggregates of platelets; instead, the macro particles grew directly into spheres dendritically. This is corroborated by the time-resolved high-resolution ultrasmall X-ray scattering performed in chapter 5. An EDS map of the entire area (Figure 6.3D) shows that the particles are predominantly Co, P, and O. A small amount of KCl is present as a byproduct of the precipitation. These SEM samples were prepared as described in the methods section.

Below the initial large spherical particles, the predominant scattering signal in the cobalt and $0.5\ \text{M}\ \text{K}_2\text{HPO}_4$ sample comes from platelets (Figure 6.3). These samples lack the sharp transition to larger, presumably spherical, macroparticles. When sectioning one of these regions for SEM imaging (Figure 6.5) we see pockets filled with disperse platelets. These platelet-filled pores are roughly the same size as the particles in Figure 6.4. The platelets again are predominantly Co, P, and O based on the EDS maps (Figure 6.5D).

The majority of the precipitants in the sample are also platelets with very little change in size or morphology. Towards the end of the diffusion front, just before there is a change in precipitant color, monodisperse spheres were identified in USAXS (Figure 6.3). The SEM images (Figure 6.6) show a mixture of platelets and monodisperse spherical particles. The particles are roughly $600\ \text{nm}$ in diameter, lack any of the same dendritic texture that was seen at the top of the gel column, and are again predominantly Co, P, and O.

Interestingly, these monodisperse particles exist in a ‘goldilocks zone’. Below this monodisperse region, the particles that precipitate are polydisperse spheres which can be seen in the lack of noticeable oscillations in the Porod region of USAXS below the ‘knee’ (Figure 6.3). SEM images also show a variety of sphere sizes (Figure 6.6B), but their low concentration makes it more challenging to accurately determine if every sphere is CoHPO_4 (Figure 6.6C), though it is possible to distinguish that the largest particles contain predominantly Co, P, and O. Also, as is the case with all EDS maps of these particles suspended in a gel matrix (Figure 6.4–Figure 6.6), determining atomic percentages is largely inaccurate. The size of the particles, and the surrounding gel matrix, makes the number of backscattered electrons very low which lowers the accuracy considerably. This is not solved by simply magnifying onto a particle of interest since number of

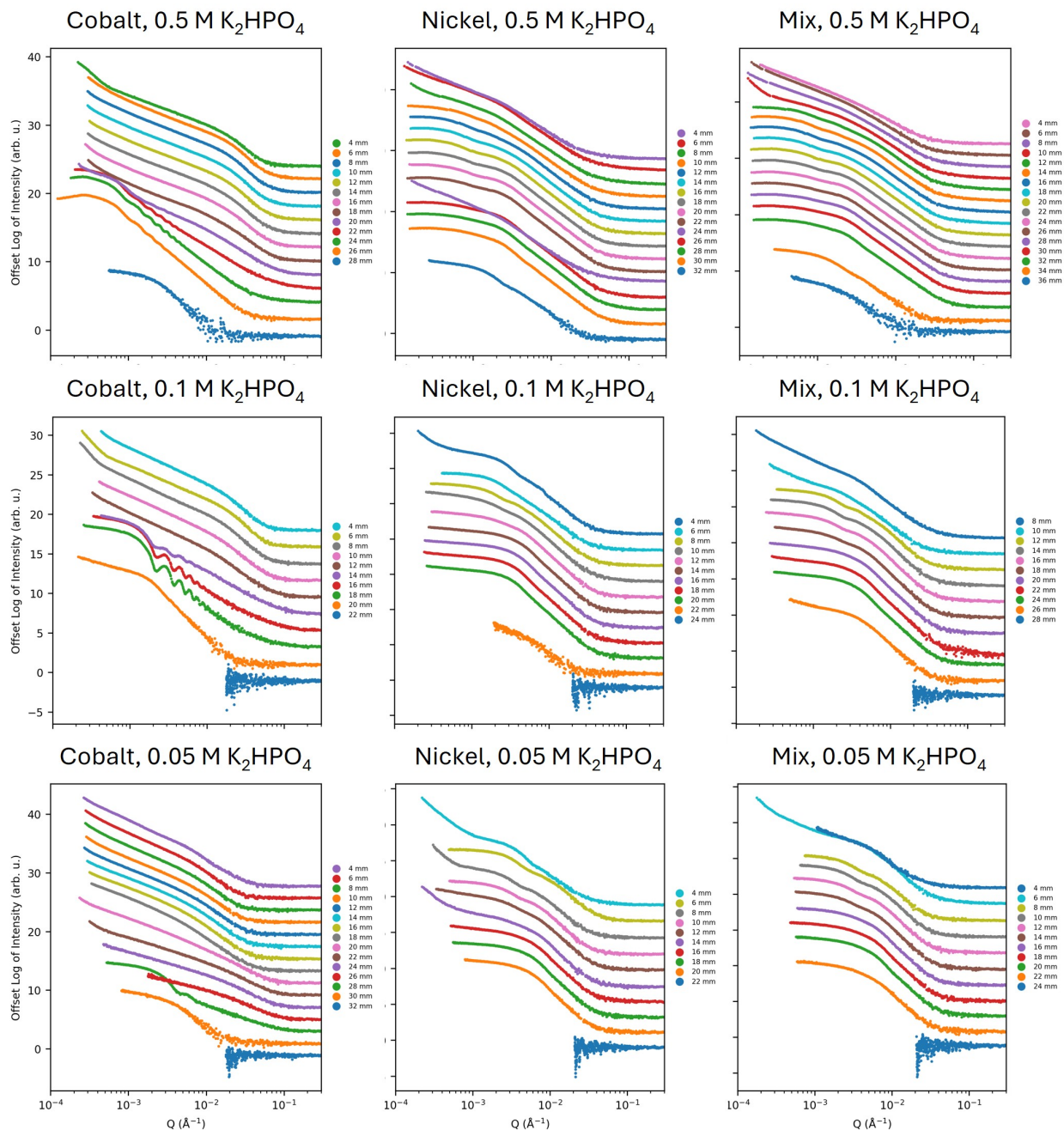


Figure 6.3: USAXS curves of 20k molecular weight PEGDA gels prepared with 0.5, 0.1, and 0.05 M K_2HPO_4 with outer electrolytes of 5 M CoCl_2 , NiCl_2 , and a 1:1 Ni:Co mix. Measurements were taken from the meniscus of the outer electrolyte (0 mm) to below the bottom of the reaction-diffusion front where outer electrolyte ions had yet to diffuse to. USAXS measurements were offset on the y-axis a fixed amount from one another.

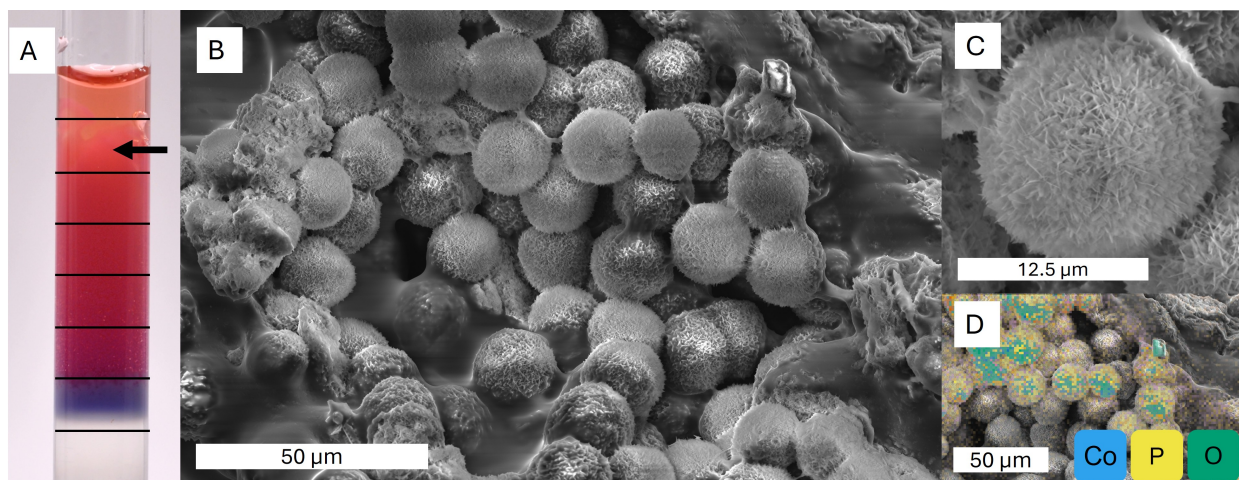


Figure 6.4: A) Image of sample prepared with 20k PEGDA and 0.5 M K_2HPO_4 using a CoCl_2 outer electrolyte with lines to indicate where the sample was sectioned. Arrow indicates which section is being imaged in the B) SEM image of the CoHPO_4 particles and C) an image of an individual particle. D) EDS map of the entire area shows that the particles are predominantly Co, P, and O.

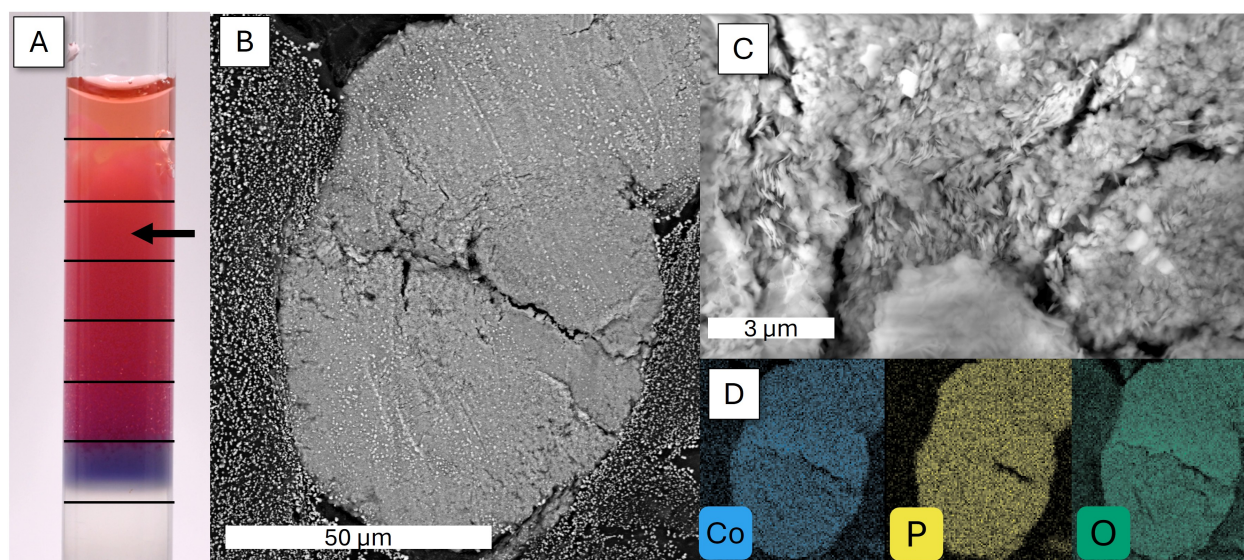


Figure 6.5: A) Image of sample prepared with 20k PEGDA and 0.5 M K_2HPO_4 using a CoCl_2 outer electrolyte with lines to indicate where the sample was sectioned. Arrow indicates which section is being imaged in the B) SEM image of the CoHPO_4 PEGDA macropore filled with C) the platelets seen in this magnified section. D) EDS map of the entire area shows that the particles are predominantly Co, P, and O.

counts per unit area remains largely the same. Also, at more intense magnifications beam damage becomes considerable which can move the particle of interest during a long scan. This is why these EDS maps should be taken more as qualitative assessments of regions of interest rather than quantitative measurements of

chemical composition.

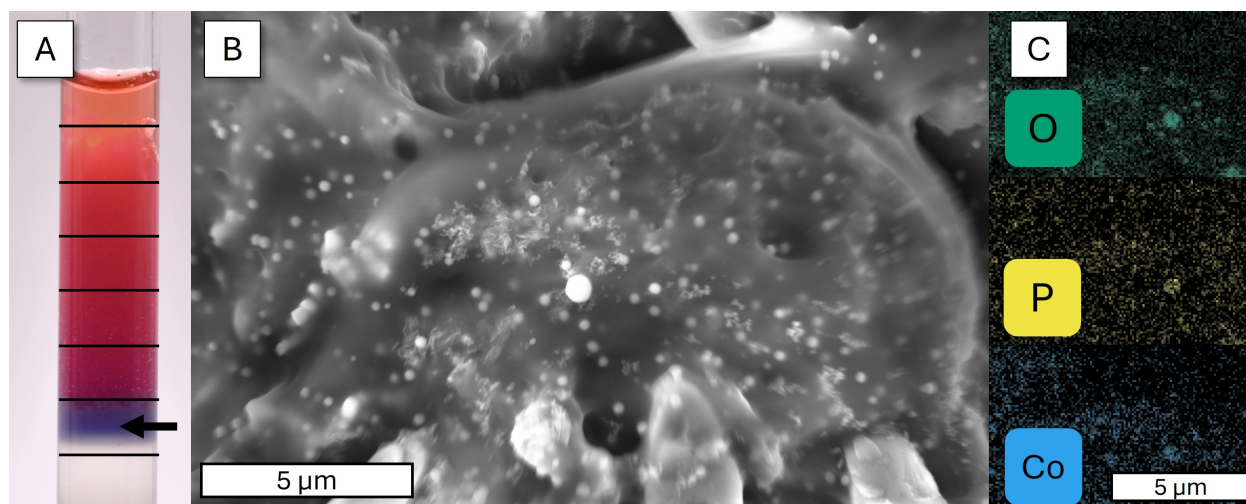


Figure 6.6: A) Image of sample prepared with 20k PEGDA and 0.5 M K_2HPO_4 using a $CoCl_2$ outer electrolyte with lines to indicate where the sample was sectioned. Arrow indicates which section is being imaged in the B) SEM image of the $CoHPO_4$ mixed monodisperse spherical and platelet particles C) the spheres seen in this magnified section and the corresponding EDS map that shows that the particles are predominantly Co, P, and O. The platelets have the same composition.

Nickel and Mixed Feedstock

Where small differences in the precipitation conditions result in large differences in particle morphology for the cobalt phosphate precipitation, the same is not true for samples with a nickel outer electrolyte, or even a 1:1 mixture of both nickel(II) chloride and cobalt(II) chloride. For the nickel(II) chloride outer electrolyte, every position along each of the samples had the same spherical morphology (Figure 6.3). These spheres are easily identified by the flat slope in the Guinier region after the 'knee'. Interestingly, a second feature is present in the nickel(II) phosphate spheres, a second 'knee' which indicates a second population of spheres. Fitting the scattering curve with a model that combines two sphere models, Figure 6.7, two populations are identified; one with a radius of 62 nm and another with 219 nm. This is roughly in line with the particles measured in a separate identical sample imaged with SEM (Figure 6.8 and Figure 6.9). Amorphous nickel(II) phosphate is also known to develop into a hollow structure over time,¹³ but the hollowing mechanism is not described in literature. Similar systems that synthesize $NiHPO_4$ undergo an Ostwald ripening process to form hollow interiors.^{17,18} These syntheses typically require elevated temperatures and ligands

to form hollow nanocrystals. The increase in size of this second smaller feature is interesting, and might be consistent with hollowing out of the particles if not for the evidence from the SEM images. Additional investigation would be required to determine the mechanism behind the preferential growth of these spheres.

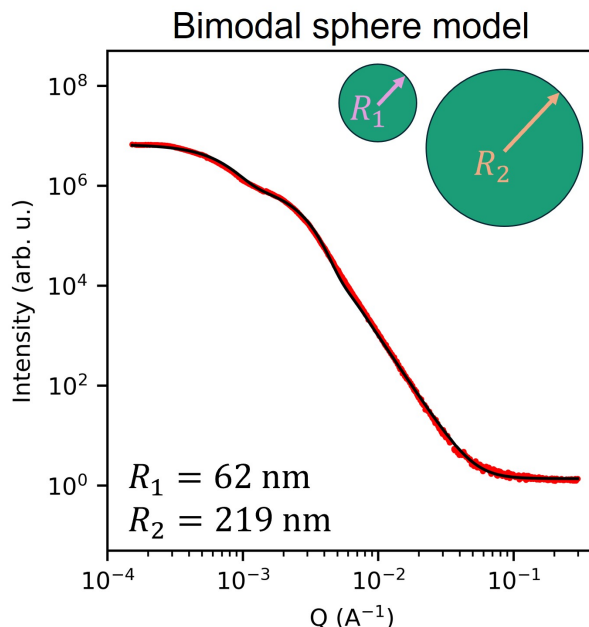


Figure 6.7: Bimodal sphere fit of the USAXS data for a sample prepared with 0.5 M K_2HPO_4 inner electrolyte and 5 M NiCl_2 outer electrolyte in 20k PEGDA, 20 mm from the top of the gel column (as seen in Figure 6.3).¹⁹

Every section of the nickel samples showed the same spherical particles that were smallest at the reaction-diffusion front and largest at the top of the gel. These samples were prepared identically to the above cobalt samples, and the gel matrix is identical; 10 wt% 20k PEGDA with 0.5 M K_2HPO_4 . The change in particle size was not as dramatic as the change in particle concentration. At the top of the gel, the particles were the most concentrated in the gel (Figure 6.8) while the density seemed to drop off in the middle (Figure 6.9) and at the bottom of the gel volume (Figure 6.10). Toward the top of the gel, where USAXS identifies there should be a bimodal distribution of particles, we do see two distinct sizes (Figure 6.8B). The largest spherical particles measure approximately 500 nm across while the smallest measure approximately 50 nm across in SEM. This matches the sizes seen in USAXS.

Moving further down the sample, this bimodal distribution seems to become less pronounced in SEM (Figure 6.9B), however the sizes of the particles match what is seen in USAXS. Unfortunately, it is difficult

to confirm this quantitatively for two important reasons. First is that imaging such as this is statistically insignificant compared to ensemble characterizations like X-ray scattering. Secondly, there are other particles present inside the gel besides NiHPO_4 , namely unreacted K_2HPO_4 and KCl byproduct. The latter being much more common towards the top of the gel. It might normally be a simple matter to single out the NiHPO_4 particles using EDS mapping, but given their relatively small size and high density, elemental maps are less useful at positively identifying which particles are which (Figure 6.8C, Figure 6.9C).

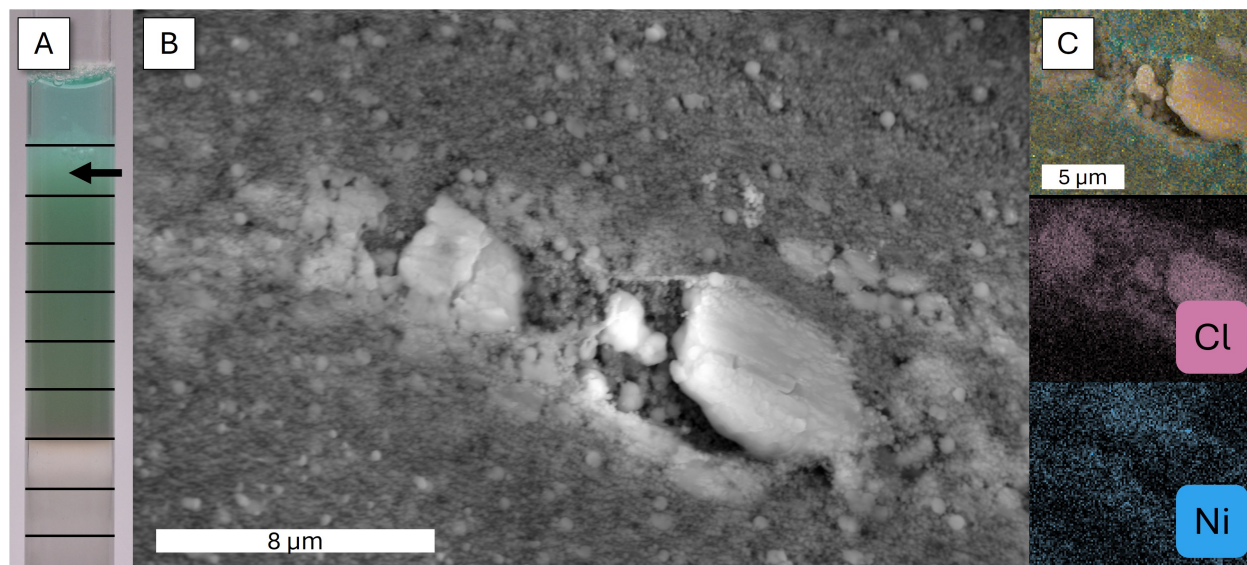


Figure 6.8: A) Image of sample prepared with 20k PEGDA and 0.5 M K_2HPO_4 using an NiCl_2 outer electrolyte with lines to indicate where the sample was sectioned. Arrow indicates which section is being imaged in the B) SEM image of the NiHPO_4 spherical particles with C) the corresponding EDS map that shows Ni and Cl rich regions is shown which shows the spheres are predominantly Nickel while the larger non-spherical particles are bulk KCl crystals.

The final position imaged in the sample was after the reaction diffusion front (Figure 6.10). Surprisingly, there were NiHPO_4 particles present at a low density in this section which were apparently low enough in concentration to not affect the color of the gel. The particles measured in SEM were similar in size to the particles measured throughout the rest of the tube. Since these particles were less densely packed into the gel than previous sections, it was also possible to identify them individually using EDS mapping (Figure 6.10C).

The naturally bimodal growth of the NiHPO_4 particles is an interesting phenomenon. This is not an uncommon phenomenon in other systems,^{20,21} and there are a number of other reported bimodalities in particle and grain sizes for specifically nickel-containing systems as well.^{22,23} The interplay between kinetics

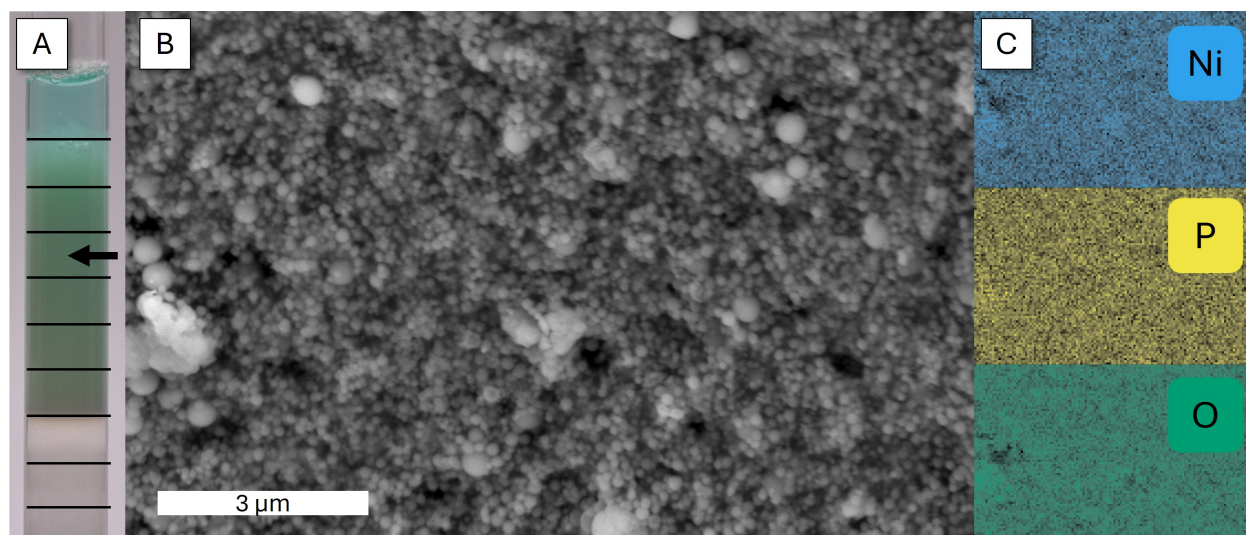


Figure 6.9: A) Image of sample prepared with 20k PEGDA and 0.5 M K_2HPO_4 using an NiCl_2 outer electrolyte with lines to indicate where the sample was sectioned. Arrow indicates which section is being imaged in the B) SEM image of the NiHPO_4 spherical particles with C) the corresponding EDS map that shows the particles are predominantly Ni, P, and O.

and thermodynamics brought on by the separation of the reagents at the beginning of the reaction-diffusion experiment is likely responsible then of inducing this phenomenon. As all of the nickel species were amorphous, it was not possible to conclude anything about the precipitants with respect to atomic structure in WAXS (Figure 6.15). It is possible that the two sizes of particles are different hydration states of NiHPO_4 which grow at different rates. The differences in hydration, similar to what was seen in the cobalt samples (Figure 6.3–Figure 6.6), could be brought on by differing reaction conditions throughout the length of the gel. A change in would not necessarily be observed for the nickel since, unlike cobalt(II) phosphates, its hydration states do not vary in color beyond shades of green.

The overarching motivation for studying the precipitation mechanism of cobalt and nickel chlorides in a hydrogel like PEGDA is to chemically separate Co^{2+} and Ni^{2+} to identify conditions that promote separation in the system. Using a mixed outer electrolyte with K_2HPO_4 as the precipitating agent, with a 1:1 molar ratio of Co:Ni at the same 5 M concentration, did not produce a noticeable separation based solely on morphology in USAXS (Figure 6.3). Instead, the morphology of the mixed case very closely resembles the same bimodal distribution of particles seen in the nickel-only outer electrolyte.

At the top of the gel there is a possible separation of cobalt and nickel. Figure 6.11 shows an SEM image

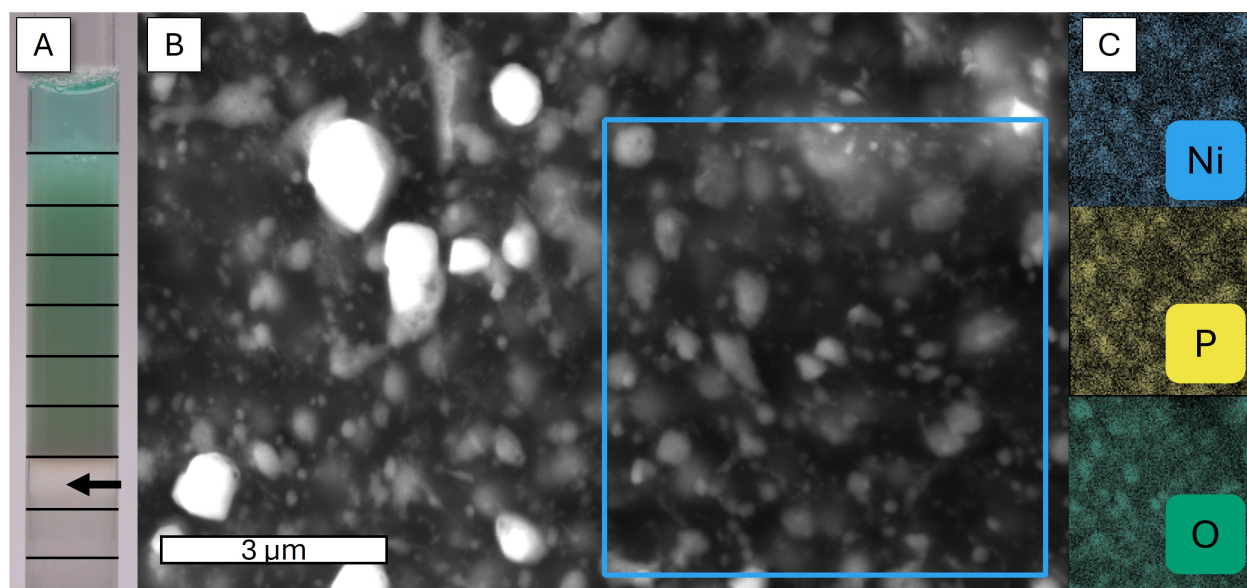


Figure 6.10: A) Image of sample prepared with 20k PEGDA and 0.5 M K_2HPO_4 using an NiCl_2 outer electrolyte with lines to indicate where the sample was sectioned. Arrow indicates which section is being imaged in the B) SEM image of the NiHPO_4 spherical particles with a blue bordered area which indicates the region where C) the corresponding EDS map was taken which shows the particles are predominantly Ni, P, and O.

of precipitants on the surface of a sample prepared using 10 wt% 20k PEGDA and 0.5 M K_2HPO_4 . The following SEM images (Figure 6.11–Figure 6.13) of the mixed outer electrolyte are of the same sample. In Figure 6.11B, a large platelet with a fissure can be seen in the background. This is one of the same platelets that were identified earlier as a cobalt-rich Co/Ni oxide (Figure 6.14, Figure 6.15). From the EDS maps (Figure 6.11C) it is difficult to identify individual particles. There is seemingly a cobalt density around the platelet, and the Ni/Co percentages were measured to be 7.6 and 9.7 atomic% (1.55×10^6 counts) respectively.

Magnifying much farther is a challenging given the low counts per second are a result of decreasing the area of interest. From SEM images of a large number of particles towards the middle of the tube, the same spherical morphology seen in USAXS is identified. Though it is difficult to say with any certainty whether there is a bimodal distribution of particles. The distribution of elements is also uniform (Figure 6.12C) with nickel and cobalt percentages of 4.6 and 5.5 atomic% respectively. This is in contrast to the top of the gel where the cobalt was higher in concentration, mainly due to the cobalt rich composite oxide.

The final position was measured just below the end of the reaction diffusion front (Figure 6.13A). There

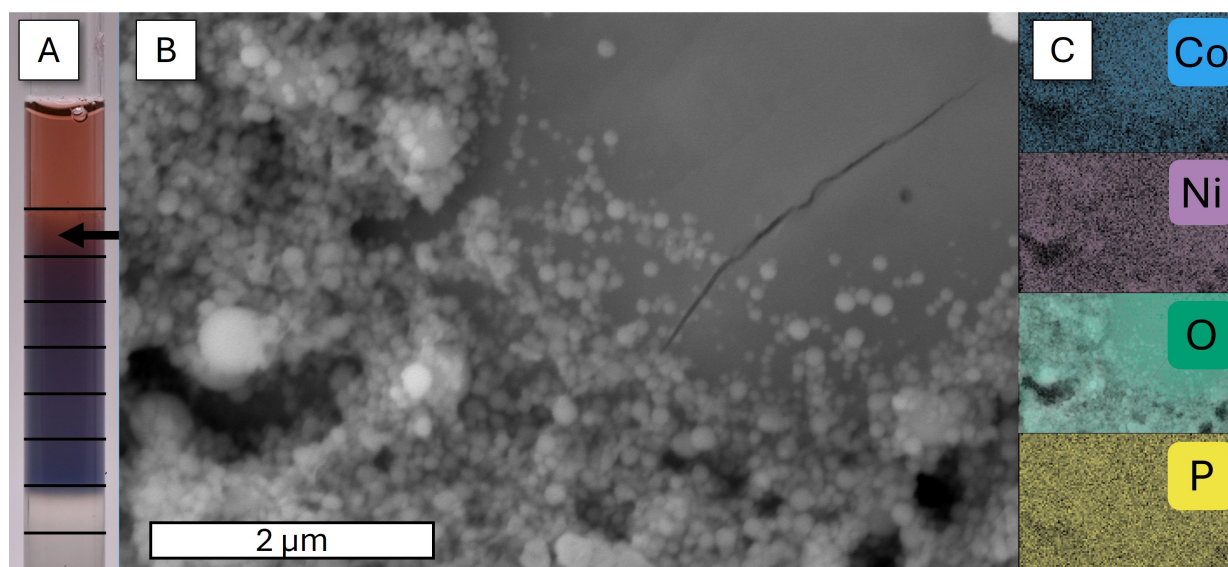


Figure 6.11: A) Image of sample prepared with 20k PEGDA and 0.5 M K_2HPO_4 using a mixed (1:1) outer electrolyte of NiCl_2 and CoCl_2 with lines to indicate where the sample was sectioned. Arrow indicates which section is being imaged in the B) SEM image of the Ni/CoHPO_4 spherical particles. A large Co/Ni oxide platelet is present in the background containing a fissure. C) The corresponding EDS map was taken which shows the particles are predominantly Co, Ni, P, and O. Cobalt, 9.7 atomic%; Nickel, 7.6 atomic% (1.55×10^6 counts).

are a variety of particle morphologies seen in the SEM image (Figure 6.13B), many of the largest particles are either K_2HPO_4 or KCl . As has been the case with all of these sections, it is difficult to isolate any individual particle with an elemental map using the Phenom Pharos. At these magnifications, beam damage can be seen as large dark voids in the center-left portion of the SEM image. While confidence in individual particle chemical identity is low, it is possible to identify a difference in cobalt and nickel concentrations. From EDS maps (Figure 6.13C) a number of particles can be seen that more have denser concentrations of NiHPO_4 compared to cobalt. Comparing the atomic percentages, nickel has a 0.692 atomic% and cobalt was measured to have 0.074 atomic%.

These results would suggest that the chemical separation was successful and that nickel was precipitated in favor of cobalt. However, atomic percentages measured in EDS in this fashion are unreliable. The atoms being measured in Figure 6.13C are below the limit of detection for the instrument, and it is difficult to ascribe them to a significant chemical separation. Also, elemental percentages are determined by modeling the histogram of inelastically scattered electron under the electron beam. Nickel and cobalt are so similar that

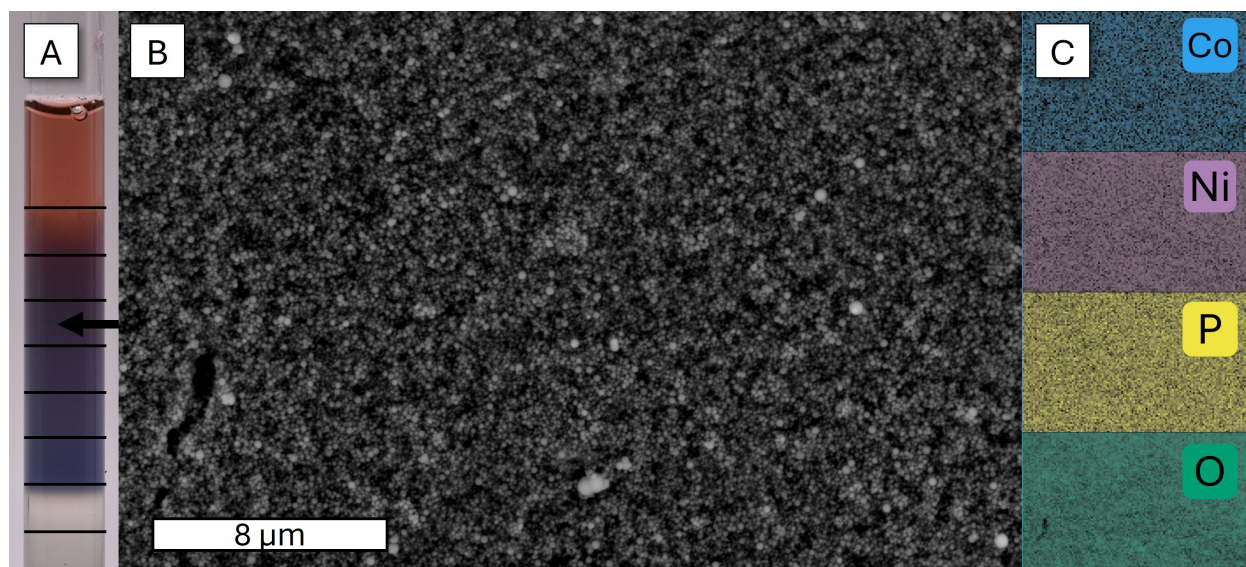


Figure 6.12: A) Image of sample prepared with 20k PEGDA and 0.5 M K_2HPO_4 using a mixed (1:1) outer electrolyte of $NiCl_2$ and $CoCl_2$ with lines to indicate where the sample was sectioned. Arrow indicates which section is being imaged in the B) SEM image of the $Ni/CoHPO_4$ spherical particles. C) The corresponding EDS map was taken which shows the particles are predominantly Co, Ni, P, and O. Cobalt, 4.6 atomic%; Nickel, 5.5 atomic% (2.19×10^6 counts).

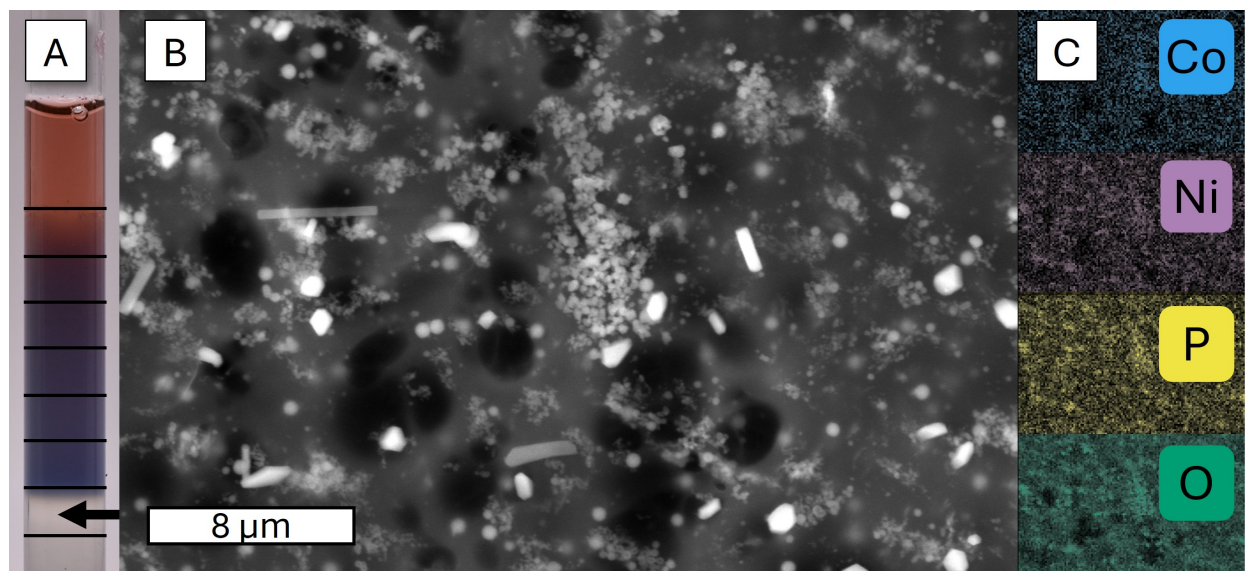


Figure 6.13: A) Image of sample prepared with 20k PEGDA and 0.5 M K_2HPO_4 using a mixed (1:1) outer electrolyte of $NiCl_2$ and $CoCl_2$ with lines to indicate where the sample was sectioned. Arrow indicates which section is being imaged in the B) SEM image of the $Ni/CoHPO_4$ spherical particles. C) The corresponding EDS map was taken which shows the particles are predominantly Co, Ni, P, and O. Cobalt, 0.074 atomic%; Nickel, 0.692 atomic% (2.11×10^6 counts).

there is only a single small peak that differentiates the two. When atomic concentrations are low, it becomes exceedingly unreliable to distinguish cobalt from nickel. It is likely that this is the reason for the discrepancy in atomic percentages in Figure 6.13. However, with respect to the higher particle concentrations seen at the top of the sample where the measured atomic percentage is higher than ~5% (Figure 6.15, Figure 6.11, Figure 6.12), this is likely a more reasonable measurement. To investigate whether or not chemical separation is achieved however, imaging will not be a sufficient technique. An elemental measurement that is either nondestructive and possible to perform with spatial resolution along the length of the sample such as Raman spectroscopy, or a technique that measures the concentration of elements in an entire sample after it is digested like inductively coupled plasmon mass spectrometry (ICP-MS). These, similar to X-ray scattering, provide a more statistically relevant measurement of the aggregate. Imaging should be used simply to inform other analyses.

6.3.3 Crystal Phases

Wide-angle X-ray scattering (WAXS) predominantly measures atomic-sized features. This makes it possible to measure atomic lattices and identify crystal phases of the precipitates. WAXS was performed at the Advanced Photon Source due to the superior resolution compared to a lab instrument. For the samples containing only the gel and any sample containing only amorphous particles, the only scattering features belong to water at these length scales.²⁴ Every hydrogel, then, along with every hydrogel containing a counter-ion, was found to have an amorphous atomic structure. This is expected as PEGDA, along with the three counter-ions investigated, NaOH, K₂CO₃, and K₂HPO₄, are all solvated in the aqueous phase. Once the outer electrolyte was added, WAXS showed that most of the precipitates were also amorphous. Despite all showing a change in color or opacity, indicating a reaction, the products of the cobalt, nickel, and mixed outer electrolytes were all amorphous when NaOH and when K₂CO₃ were the counter ions.

There was, however, one instance of crystalline particles, which occurred only in the mixed samples and only at the very top of the gel. Select SAXS measurements at these points in 700 molecular weight PEGDA (Figure 6.14) show a Guinier region with a power law slope of approximately -2 which indicates large flat structures, like platelets.²⁵ The scattering curves were fit with a Guinier-Porod model where the Porod exponent was fixed at a value of 4, keeping in line with a solid particle.²⁶ The radius of gyration,

R_g , for a platelet is related to the thickness by $T = R_g\sqrt{12}$ where T is the thickness. The thickness of the platelets varied from sample to sample but was approximately between 15 and 40 nm. The dimension variable, s , for the fits was approximately 2, which is in line with a platelet morphology as well. The same structures are present in every sample with a mixed outer electrolyte, and only the mixed outer electrolytes, regardless of PEGDA or counter ion identity. This suggests that the precipitate is not a product of any counter ion's reaction with cobalt and nickel. No oxide of cobalt(II) and nickel(II) fits these Bragg peaks, so the most likely phase is a cobalt(II) and nickel(II) chloride hydrate that precipitated out of the concentrated solution.

For one of the samples containing a mixed outer electrolyte (Figure 6.15A) SEM images and EDS maps were taken of the large flat precipitates at the top of the gel. The sample itself was made of 20k PEGDA and had a K_2HPO_4 concentration of 0.5 M. Given that the USAXS curves for every sample deviated very little, this is assumed to be a good representative for most samples. The SEM image (Figure 6.15B) confirms that the structures have large flat surfaces and are incredibly thin. The particles themselves are leaf-shaped.

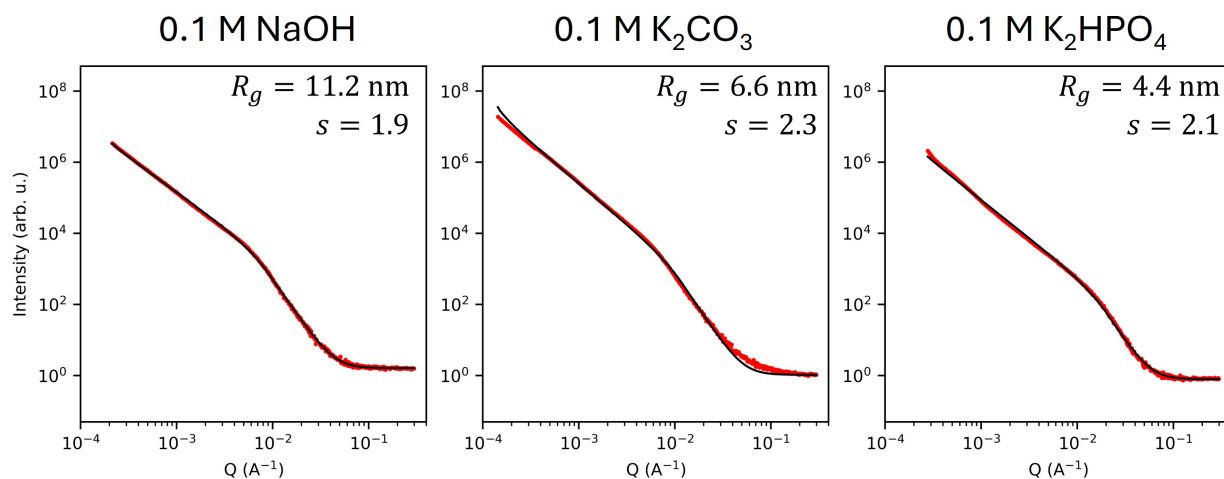


Figure 6.14: Ultrasmall angle X-ray scattering measurements were made at the top of 700 molecular weight PEGDA gels prepared with a 0.1 M concentration of the three outer electrolytes, NaOH, K_2CO_3 , and K_2HPO_4 . All used a mixed outer electrolyte of 5 M $NiCl_2$ and $CoCl_2$. Both axes in log scale. The plotted black line is the scattering modeled with a Guinier-Porod model with the Porod exponent kept at 4, which is physically representative of a solid precipitate.²⁶ The radius of gyration, R_g , and the dimension variable, s , are included.

While the thickness of the leaf shaped particles is difficult to measure in SEM because of how thin they are, and the limits of the instrument, they are thin to a degree that they are transparent to the 10 kV electron

beam at the tips and edge. It is not possible to measure the longer dimensions with scattering since the features are too large. In EDS, Figure 6.15C, the chemical identity of the platelets is predominantly cobalt, nickel, and oxygen. These platelets do not contain phosphorous as can be seen by the even distribution of phosphorous counts. When measuring the spectrum at a smaller selected area on the surface of a platelet, the ratio of Co:Ni was found to be approximately 1.8:1. The amount of oxide is difficult to reliably measure in this way due to the amount of oxygen in the surrounding polyethylene glycol, as well as what is present from general contamination. It is likely that these platelets, considering that they formed only at the top of the gel, in mixed electrolytes, and in the same morphology and phase irrespective of the type of inner electrolyte, are a cobalt/nickel dichloride hexahydrate. This would be possible given the high concentration of the electrolyte solution. No matter the mechanism, these initial measurements show promise that it may be a useful way to concentrate cobalt away from nickel in a separation process.

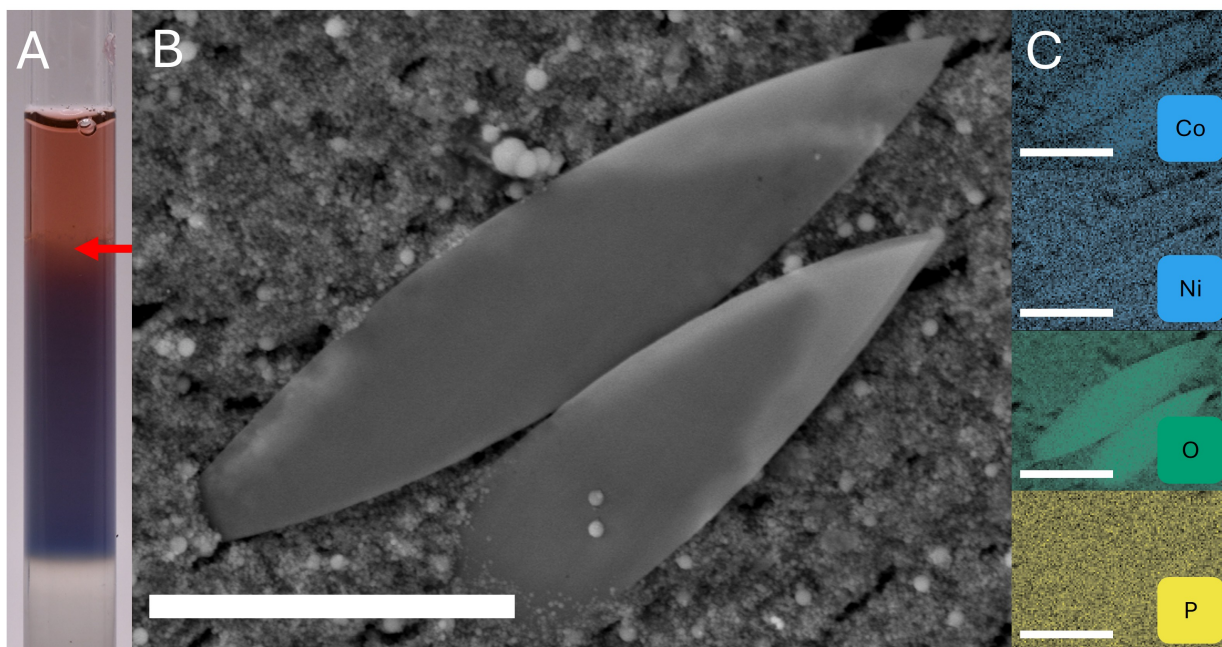


Figure 6.15: A) Photograph of a reaction-diffusion sample inside a 5 mm OD NMR tube with a mixed NiCl_2 and CoCl_2 outer electrolyte (5 M) on top of the 20k molecular weight PEGDA gel prepared with 0.5 M K_2HPO_4 . The red arrow marks approximately where the B) SEM image of large platelets among smaller spherical particles was taken along with corresponding C) EDS maps of the same area of interest. All scale bars (white) are 10 μm .

These platelets were the only identifiable ‘impurity’ in WAXS that was not the product of a reaction between the outer electrolyte and a counter ion. As previously stated, most reaction products were amorphous.

An exception however, was CoCl_2 outer electrolyte reacted with K_2HPO_4 which produced several crystalline phases (Figure 6.16). NiCl_2 outer electrolyte did not produce any crystalline phosphate phases, but interestingly, the mixed outer electrolyte did. In very low intensities, and only in upper sections of the gel, $\text{Ni}_2(\text{PO}_4)_3 \cdot 8\text{H}_2\text{O}$ was found in the naturally occurring monoclinic phase known as arupite (Figure 6.17). This phase was only discernible in the highest concentration of K_2HPO_4 . The intensity of these Bragg peaks relative to the those with the CoCl_2 outer electrolyte was drastically lower indicating that the majority of the outer electrolyte was not converted to a crystalline phase.

For the cobalt phosphate phases, there are definite changes throughout the length of the gel, such as a change of color at the leading reaction-diffusion edge, which correspond to structural changes identified in WAXS from amorphous to crystalline (Figure 6.16). This has been previously reported transition in the precipitation of cobalt using phosphates.²⁷ Using WAXS alone gives little confidence in the identity of the phase as the difference between the orthorhombic $\text{Co}_2(\text{PO}_4)_3 \cdot 8\text{H}_2\text{O}$ and monoclinic $\text{CoHPO}_4 \cdot 3\text{H}_2\text{O}$ in this q range is subtle given the peak broadening in WAXS. The identifying peaks are much more clear in the SAXS region, which chapter 5 explores more thoroughly.

6.4 Discussion

A wide reaction space was sampled using reaction-diffusion coupling through PEGDA hydrogels. This method revealed a number of phenomena associated with the precipitation of nickel and mixed cobalt/nickel feedstocks. The most significant behavior that was identified was the change in crystal morphology with mixed feedstocks. A mixed feedstock did not produce separate precipitates of distinct cobalt and nickel, instead the crystallization proceeded similar to nickel alone. It could be inferred from the lack of crystalline cobalt or the separation of cobalt and nickel that the two precipitated in a mixed Co/Ni amorphous phase. An identical behavior in the related crystallization of cobalt and nickel mixtures with dibasic ammonium phosphate to a struvite phase was identified by Karafiludis *et al.*¹³ Given the similar chemistries of cobalt(II) and nickel(II), it is likely that the cobalt and nickel are precipitating together as an amorphous cobalt/nickel phosphate at roughly the same time. Since there is a lack of crystallinity, it is unlikely that cobalt is precipitating separately, as $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ is crystalline. While in a different ammonia-containing system, mixed species investigated by Karafiludis *et al.* identified that isostructural cobalt(II)

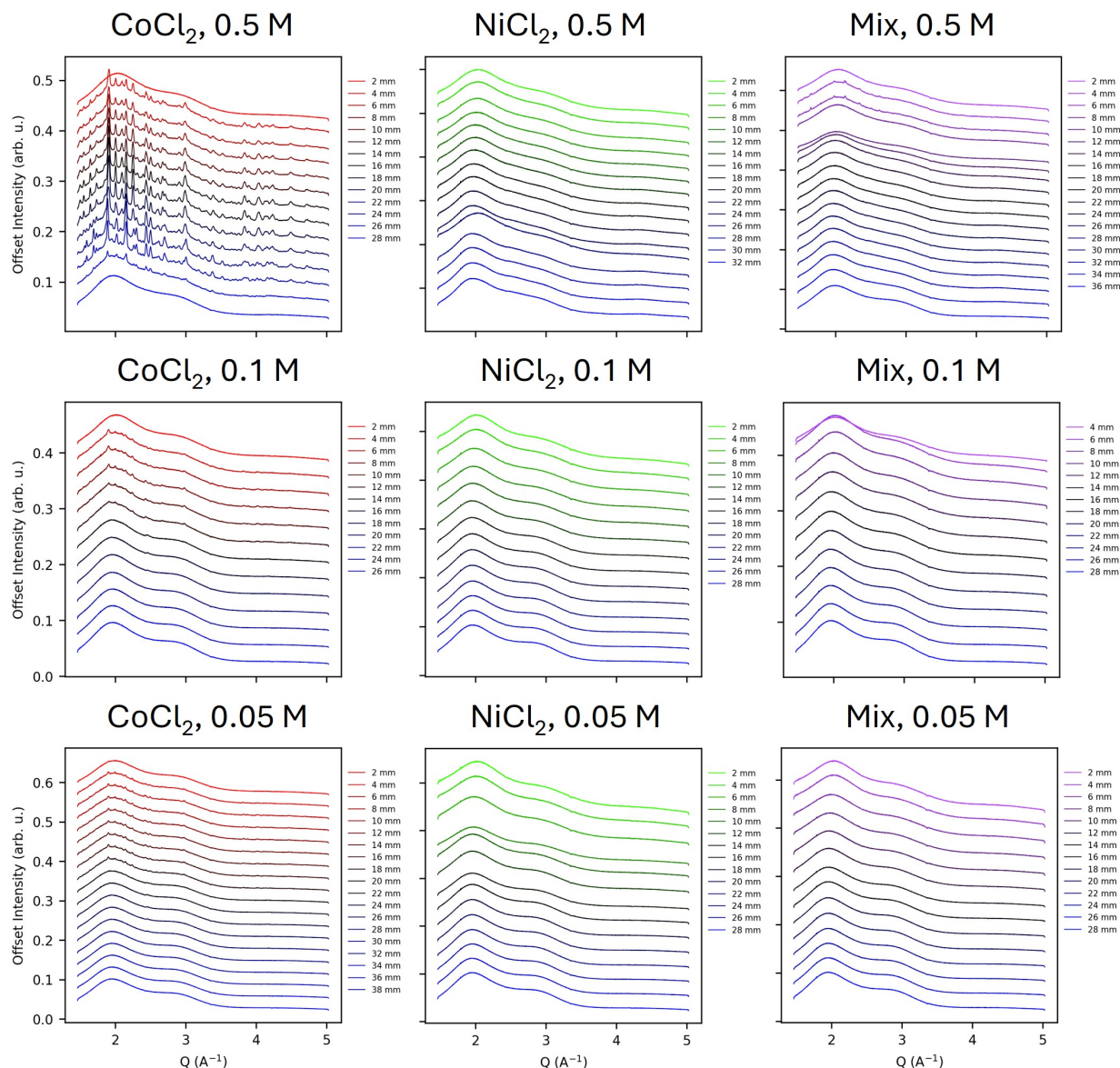


Figure 6.16: Wide angle X-ray scattering measurements of reaction-diffusion samples prepared with 20k molecular weight PEGDA and a concentration K_2HPO_4 , stated in plot titles, with 5 M aqueous outer electrolytes of $CoCl_2$, $NiCl_2$, or a 1:1 mixture of both $CoCl_2$ and $NiCl_2$, the outer electrolyte identity also being stated in the plot titles. Measurements were taken over the length of the sample from the top of the outer electrolyte (0 mm) to the bottom of the reaction-diffusion front. USAXS measurements were offset on the y-axis a fixed amount from one another.

and nickel(II) phosphates form with a cobalt-rich core and nickel-rich shell.¹³ This would be confirmed by identifying individual particles that have both nickel and cobalt present in an EDS map, which would be possible in TEM with a small number of particles extracted from the gel.

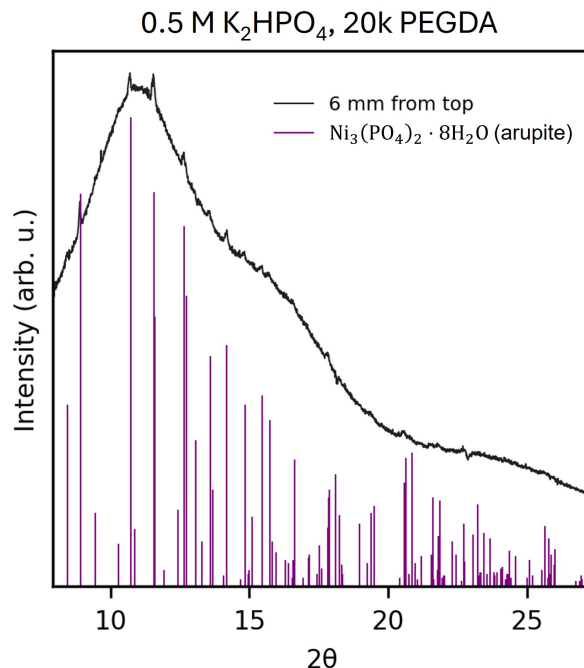


Figure 6.17: Wide angle X-ray scattering curve taken 6 mm from the mixed outer electrolyte (1:1 Ni:Co) meniscus of a sample prepared with 0.5 M K_2HPO_4 in a 20k PEGDA (10 wt%). Phase is monoclinic arupite with formula $\text{Co}_2(\text{PO}_4)_3 \cdot 8 \text{H}_2\text{O}$

One of the benefits of reaction-diffusion coupling in hydrogels is the relationship between the reaction and the rate of diffusion. Cobalt(II) chloride and nickel(II) chloride are incredibly similar in terms of their rates of diffusion. This is exemplified by their similar measured effective propagation rates in Figure 6.18 when reacting with 0.1 M K_2HPO_4 . When using a mixed outer electrolyte, however, the effective propagation rate of the front was noticeably faster at $D = 7.46 \times 10^{-6} \text{ cm}^2/\text{s}$ compared to 5.00×10^{-6} and $5.25 \times 10^{-6} \text{ cm}^2/\text{s}$ for cobalt(II) and nickel(II) respectively. The simulation results in Figure 5.1 showed that the propagation rate is affected by the relative concentration (or chemical activity) and the molecular diffusivity of the reagents. Since the gel is the same between these three samples and all have the same concentration, the difference in the propagation rate could be from the difference in the reaction. From literature, we know that it is possible for a mixture of cobalt(II) and nickel(II) to follow a crystallization path with slower kinetics than pure cobalt(II) or nickel(II).¹³ The faster propagation that we observe may indicate that the reaction is not third order with the metal ion as we predict, but obeys a lower order dependence. This would make the driving force of the diffusion greater, as fewer metal ions would be consumed, leading

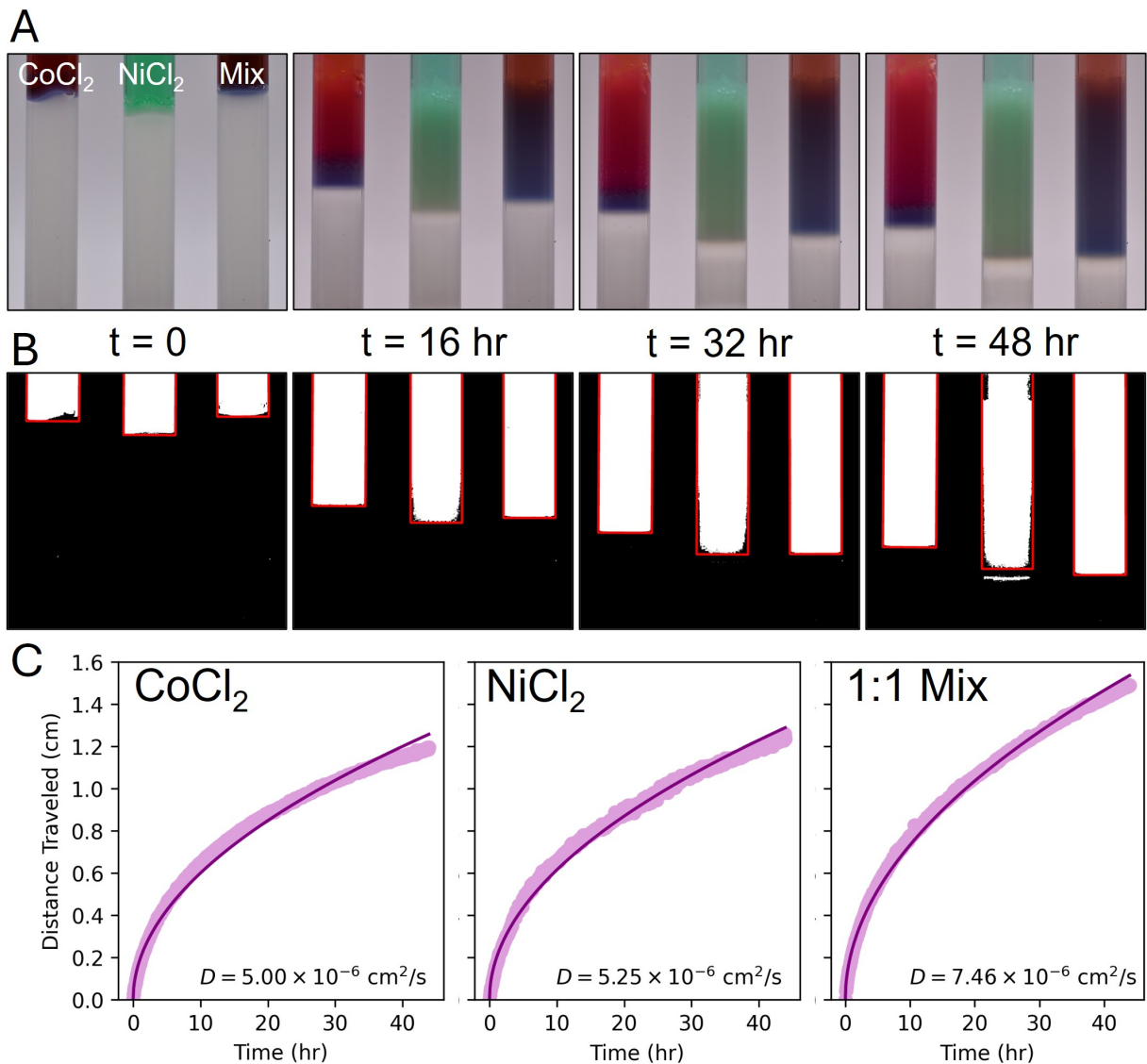


Figure 6.18: **A)** Timelapse images over 48 hours of samples with 5 M outer electrolytes of CoCl₂ (left), NiCl₂ (middle), and the mixture of both NiCl₂ and CoCl₂ (1:1) diffusing and precipitating into three identical volumes of 20k molecular weight PEGDA hydrogel prepared to have a 0.5 M concentration of K₂HPO₄ as the inner electrolyte. **B)** Binary masks (images with RGB values of either 0 or 255) of the above timelapse with identified high contrast areas marked by computer vision (OpenCV) with a parameterized red box to track diffusion. **C)** Plots of the position over time of the three different outer electrolytes in identical gels. The light purple data points are fit by the dark purple curve with a mean square displacement, $x(t) = \sqrt{2Dt}$, to recover an effective propagation rate, D . This effective propagation rate is given in the bottom of the plots.

to a steeper concentration gradient throughout the gel volume.

6.5 Conclusion

Reaction-diffusion coupling in PEGDA hydrogels was used to expose a wide parameter space to interrogation with X-ray scattering and electron microscopy. This made it possible to identify a number of unique phenomena that occupied small local minima within the larger parameter space, such as the formation of large cobalt/nickel crystals above gels and specific conditions like the crystallization of nickel and cobalt with K_2CO_3 in PEGDA which produced a wide range of particle sizes depending on the molecular weight of the gel. This phenomenon deviated from the behavior of all other counter ions and may point to an opportunity to direct the crystallization using the gel structure where it was agnostic to the structure in most other cases. We also were able to see the repeated development of a bimodal distribution of nickel and cobalt/nickel mixed precipitates when using K_2HPO_4 as the counter ion. Given that in chapter 5 we identified that cobalt(II) phosphate crystallization is driven by dissolution and reprecipitation, the bimodal distribution of nickel(II) containing particles could be pointing to preferential ripening of one species over another, which would be greatly beneficial to the separation of cobalt and nickel. We find a similarly interesting phenomenon in the NaOH system where developing morphologies point to nickel precipitating first in the gel column, followed by cobalt. Altogether, this data lays a firm foundation for future, more targeted experiments in the cobalt/nickel reaction-diffusion system.

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Chapter 7

Conclusion

At some point in the not-too-distant future, we must contend with the simple fact that renewable energy is a materially expensive problem. As we free ourselves from fossil fuels, it is equally important that we ensure the diversification of our supply chain through substitution and recycling. In this thesis, we contributed solutions regarding the replacement and recycling of critical materials for the transition to cleaner, more sustainable sources of energy. The technology that is currently perhaps most central to the discussion surrounding clean energy and critical materials is the lithium-ion battery. To make batteries a more attractive mode of energy storage, it is important to explore alternative materials that can provide diversity to battery architecture. To this end, in chapter 4 we developed a synthesis for ultrasmall Sb_2S_3 nanoparticles that can be performed in less than a minute at room temperature, in open air, using readily available reagents. These nanoparticles exhibit interesting spontaneous assemblies in solution that were driven by their size and the choice of ligand. By changing the type of ligand and the concentration, the assembly was shown to be tunable. The electrochemical performance of the nanoparticles was also extremely impressive and found to be affected significantly by the choice of ligand, despite having been removed before cycling. This work demonstrates the need for a more systematic understanding of the ligand's effects on nanosized electrochemical materials.

While diversifying the available materials for new battery chemistries is an improvement, the more important, and significantly more challenging, problem to overcome is making sure that the elements we currently use remain in the material economy for as long as possible through recycling. To make widespread

recycling of our batteries and magnets a reality, robust and economically feasible recycling strategies are required. Expanding our toolset for understanding crystallization mechanics would aid this for hydrometallurgical extraction systems. In chapter 5, we demonstrated the utility of reaction-diffusion coupling in hydrogels to produce a wide array of morphologies in the cobalt(II) phosphate system, revealing important conclusions about its crystallization. The precipitates were investigated *in situ* using X-ray scattering to efficiently determine morphology, size, and crystal structure. We spatially and temporally mapped the crystallization of cobalt(II) phosphate in hydrogels from amorphous species and metastable monoclinic intermediates to the final orthorhombic structure, and reported the gel dependence on crystal morphology. The hydrogel also allowed us to discern that the driving force of the crystal transformations was dissolution and subsequent reprecipitation, given that the convective aggregation had been eliminated by the gel.

To extend the reaction-diffusion methodology beyond the single-component cobalt(II) chloride system, we also investigated the crystallization of nickel(II) and nickel/cobalt mixed feedstocks in hydrogels in chapter 6. X-ray scattering for analyzing crystallization was used to assess the precipitation of feedstocks with cobalt(II), nickel(II), and a mixture of the two ions. We found with this in-progress direction that the crystallization of mixed feedstocks behaves differently than cobalt or nickel alone. Given that the hydrogels are a highly separative environment due to the large number of supersaturation conditions throughout the gel, we were able to efficiently rule out a number of reaction conditions and identify others that show promise. It also exposed novel behaviors in the precipitation of bimodal distributions of nickel(II) phosphate particles as well as the precipitation of large mixed cobalt and nickel crystals.

Appendix A

Appendix

A.1 Characterizing Reaction-Diffusion Coupling with X-ray Scattering

A.1.1 Cobalt(II) Phosphate Precipitation in Hydrogels

Changing polyacrylamide structure does not affect precipitation behavior

There were some differences in particle sizes between polyacrylamide prepared at 10 and 15 wt% when using K_3PO_4 as the inner electrolyte. Comparing Figure A.1C and Figure 5.4C, both formed precipitates of approximately the same size, 104.1 nm for 10 wt% T and 90.4 nm for 15 wt% T, and in both a second population of larger domains formed in the middle of the gel column. This second feature is too large to be seen in HR-USAXS for the 10 wt% sample (Figure 5.4C), but is an order of magnitude smaller in the 15 wt% sample and can be identified as spheres based on the flattened Guinier region (Figure A.1C). These spheres are 1,390 nm in diameter, while the smaller population remains the same size within error of the fit (87.0 nm).

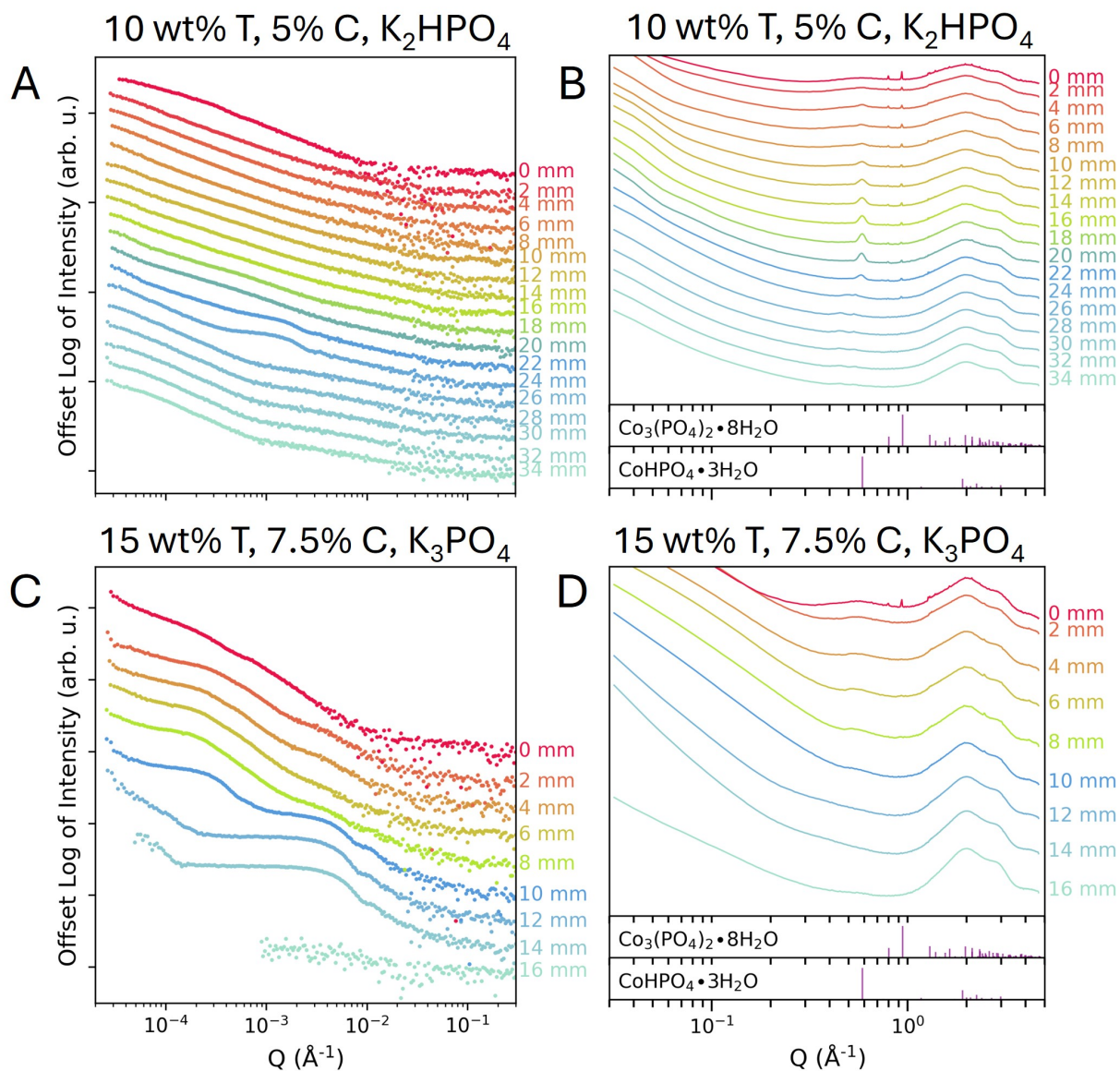


Figure A.1: HR-USAXS and SAXS/WAXS of polyacrylamide reaction-diffusion samples prepared with a 5 M CoCl_2 outer electrolyte and a 0.1 M inner electrolyte. First sample was prepared with 10 wt% total monomer (T) and 5% crosslinker with 0.1 M K_2HPO_4 and measured with **A)** HR-USAXS and **B)** SAXS/WAXS. The second sample was prepared with a 15 wt% total monomer (T) and 7.5% crosslinker and measured with **C)** HR-USAXS and **D)** SAXS/WAXS as well

Time-dependent USAXS reveals spheres decrease in diameter and number during crystallization

The time-dependent USAXS measurements demonstrate that the crystallization proceeds *via* dissolution and reprecipitation (Figure A.2). The scattering was fit with a spherical model so that the dissolution could be

followed quantitatively (Figure A.3).

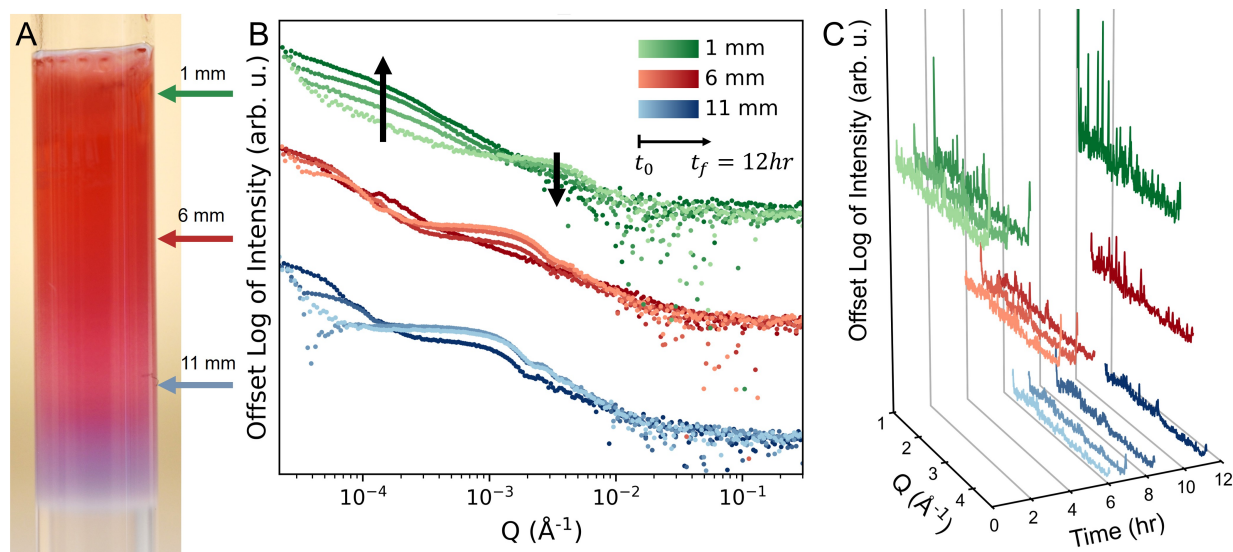


Figure A.2: **A)** Image of reaction diffusion sample, 5 M CoCl_2 outer electrolyte removed, using 10 wt% polyacrylamide gels (5% crosslinker) prepared with 0.1 M K_2HPO_4 . Colored arrows mark the measurement positions in the sample at 1 mm (green, top) 6 mm (red, middle) and 11 mm (blue, bottom). **B)** HR-USAXS (3 min measurement) over a 12-hour period of the same three positions in the sample (1, 6, and 11 mm). Lighter colors are earlier and darker colors are later in experiment window. **C)** WAXS (30 sec measurement) taken immediately after each HR-USAXS measurement. To attempt to follow the reaction-diffusion front, measurements at the three positions were staggered and followed by a final measurement at the end of the experiment. USAXS and WAXS plots are offset from one another on the y-axis a fixed amount depending on the position they were measured at (1, 6, or 11 mm). No additional offsets were applied for measurements made at different times.

1 mm, the average particle diameter is 109 nm; at 6 mm, the spheres are 272 nm; and at 11 mm, they are 435 nm. For the 1 and 6 mm positions, the sphere feature eventually disappears, making it impossible to fit and identify a trend. The 11 mm position does show the sphere diameter increasing from 402 nm to a maximum of 467 nm before decreasing in diameter at the final measurement to 443 nm (Figure A.3). This trend could coincide with growth followed by dissolution of the small spheres. If the reaction had not occurred inside a gel, the growth of the features in lower q might indicate aggregate. However, this behavior is consistent with dissolution and re-precipitation rather than aggregation since the gel prevents the transport of the relatively large precipitates required for aggregation to occur. This is corroborated by SEM images (Figure 5.2C) where particles are seen to be separated without any aggregation.

Even though the individual HR-USAXS curves are in an absolute scale, it is not possible to measure

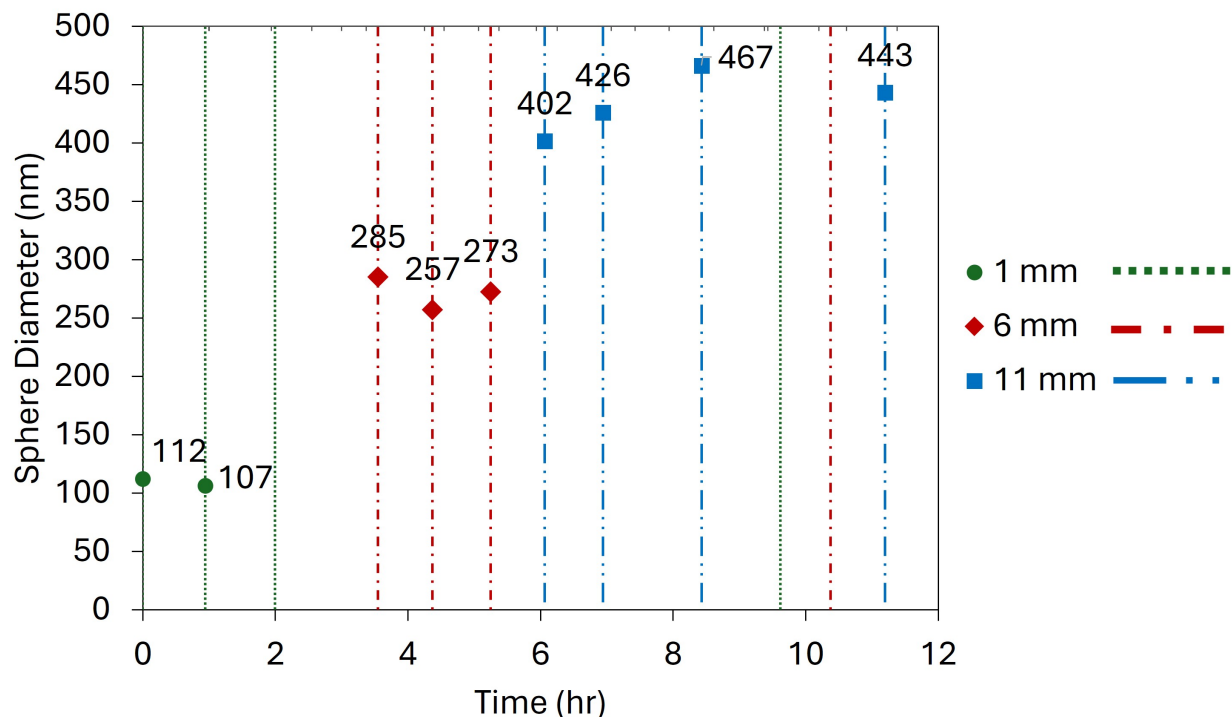


Figure A.3: Fitting results of HR-USAXS data of the reaction diffusion sample in Figure 5.5 with a 5 M CoCl_2 outer electrolyte, a 0.1 M K_2HPO_4 inner electrolyte in a 10 wt% polyacrylamide gel (10 wt% T, 5 %C). Scattering profile was fit with a hard sphere model without structure or polydispersity.¹ The vertical dotted lines indicate the times when a measurement was taken at that position. Measurements with a vertical line but without a point indicate where the number of spherical particles had decreased enough so that it was unable to be fit with the spherical model.

the volume fraction of the sphere, platelet, and microsphere populations from these experiments since the concentration of the reagents throughout the gel is not uniform due to the reaction-diffusion process. The transport of the outer electrolyte into the gel prevents there being a closed-system, which makes an estimate of the ratios between the populations highly inaccurate.

Additional time-resolved SAXS/WAXS measurements of 20k PEGDA gels were made using the Xenocs Xeuss 3.0 at the University of Washington, which can be seen in Figure A.4. The sample was prepared with a 5 M CoCl_2 outer electrolyte and a 0.1 M K_2HPO_4 inner electrolyte inside the 10 wt% PEGDA. The lab-scale Xenocs instrument uses a Cu X-ray source (1.54 Å, 8.05 keV) with a flux of around 5×10^8 photons/s compared to the 21 keV and 1×10^{12} photons/s at the Advanced Photon Source. Because of this, a thinner sample was required, and only the largest, most broad peaks were discernible. Regardless,

it can be seen that at the three positions in the gel that were measured (2, 6, and 12 mm from the top of the gel) the same monoclinic $\text{CoHPO}_4 \cdot 3\text{H}_2\text{O}$ phase was present in different concentrations. Over time, each position in the gel goes through the same crystallization pathway, starting amorphous, then monoclinic $\text{CoHPO}_4 \cdot 3\text{H}_2\text{O}$ and finally orthorhombic $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ which can be understood from the appearance and disappearance of the broad peak at $0.6 \text{ \AA}^{-1}$. From the different relative intensities of the $0.6 \text{ \AA}^{-1}$ peak at the three positions, we can tell the concentration of the monoclinic phase is different depending on where in the gel the crystallization is occurring. This suggests that the crystallization can be controlled by the position in the gel and the unique supersaturation environment at each distinct position.

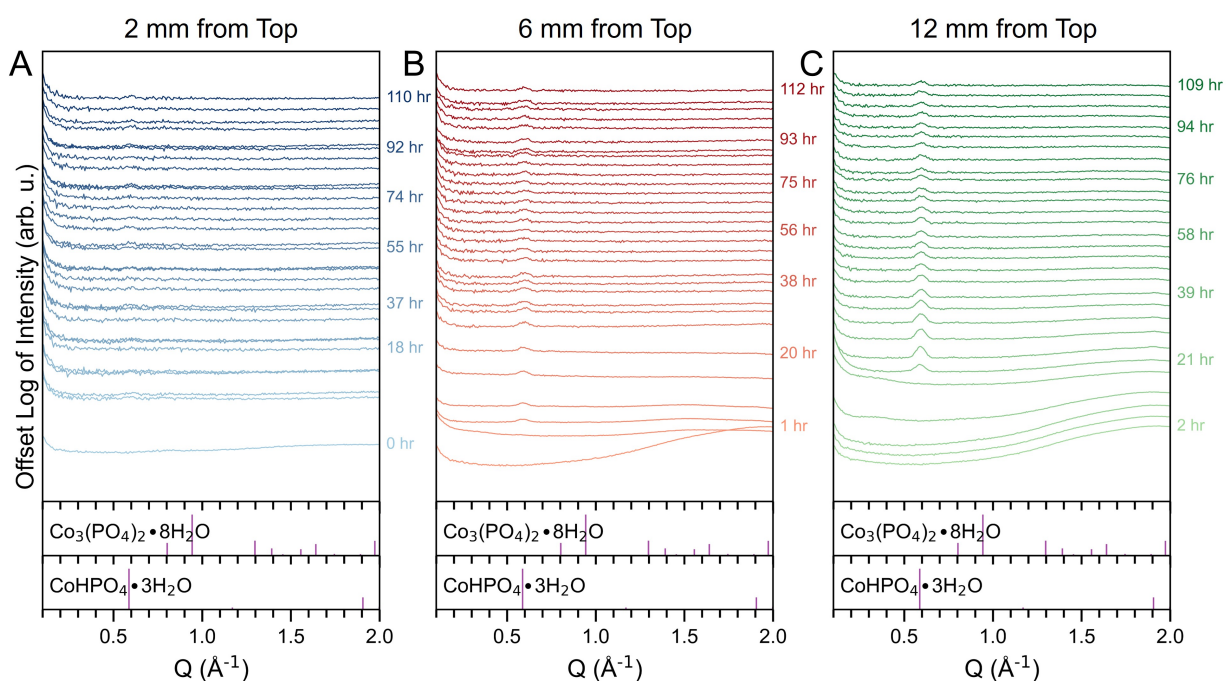


Figure A.4: A reaction-diffusion sample prepared with a 5 M CoCl_2 outer electrolyte and a 0.1 M K_2HPO_4 inner electrolyte in 20k molecular weight PEGDA (10 wt%). Wide-angle X-ray scattering using a Xenocs Xeuss 3.0 at the University of Washington was measured **A)** 2 mm from the top of the gel, **B)** 6 mm from the top of the gel, and **C)** 12 mm from the top of the gel. Samples were prepared in thin-walled (10 μm) 1.5 mm diameter quartz capillaries purchased from Hampton Research (Aliso Viejo, CA) and sealed with two-part 5-minute epoxy from Devcon (Illinois Tool Works; Danvers, MA). WAXS plots are offset from one another on the y-axis a fixed amount from one another.

A.1.2 Mixed Co^{2+} and Ni^{2+} Precipitation in Hydrogels

Shorter PEGDA hydrogels scatter in USAXS measurements

In chapter 6, the shorter PEGDA hydrogels are not featureless in the USAXS measurements. From SAXS (Figure A.15), the nano-sized features can be resolved, but the USAXS region can discern the larger voids and structures.^{2,3} The scattering profile for the longer PEGDAs is a flat, noisy curve since these samples have a very low scattering length density compared to the sample container at low q . The shorter PEGDAs likely have larger voids and more rigid structures, which scatter more prominently.⁴ USAXS at the APS in Argonne National Lab uses a Bonse-Hart USAXS configuration, which has a relatively low signal-to-noise ratio at the high end of its q range due to parasitic backscattering from imperfections in the rocking crystal.⁵⁻⁷

Samples prepared with 0.05 M NaOH and K_2CO_3 gelled but had low signal

For 0.05 M NaOH (Figure A.6), the cobalt and mixed outer electrolytes did not present a significant amount of signal above the background. In the nickel samples, there is similarly poor signal above background in the range of $10^{-3} \text{ \AA}^{-1}$ to $2 \times 10^{-2} \text{ \AA}^{-1}$. A discernible Guinier region below $10^{-3} \text{ \AA}^{-1}$ is present, however, which puts the size of these particles at approximately 650 nm. The poor sampling of this scattering data makes a model less useful. The measurement at 4 mm of the mixed case does, however, show an identical morphology to the large leaf-like platelets found in mixed samples that were discussed previously. Large structures can be seen in the nickel sample as well, as evidenced by the slope out to the low- q region at 4 and 6 mm. These lack a Guinier region like what can be seen in 4 mm in the mixed sample and features a power law slope of -2.45, so it is likely that this is a large fractal aggregate whose size is outside the instrument q range.⁸

Using a low concentration of potassium carbonate had a similar effect. The combination of 700 molecular weight PEGDA and 0.05 M K_2CO_3 did not produce a high concentration of precipitates (Figure A.7). Increasing the counter ion concentration to 0.1 M increased the number of scatterers and made more features distinguishable.

Increasing the molecular weight of the gel from 700 to 4k g/mol does not result in the same precipitation behavior. The most prominent difference is that the scattering intensity stays the same for 700 PEGDA

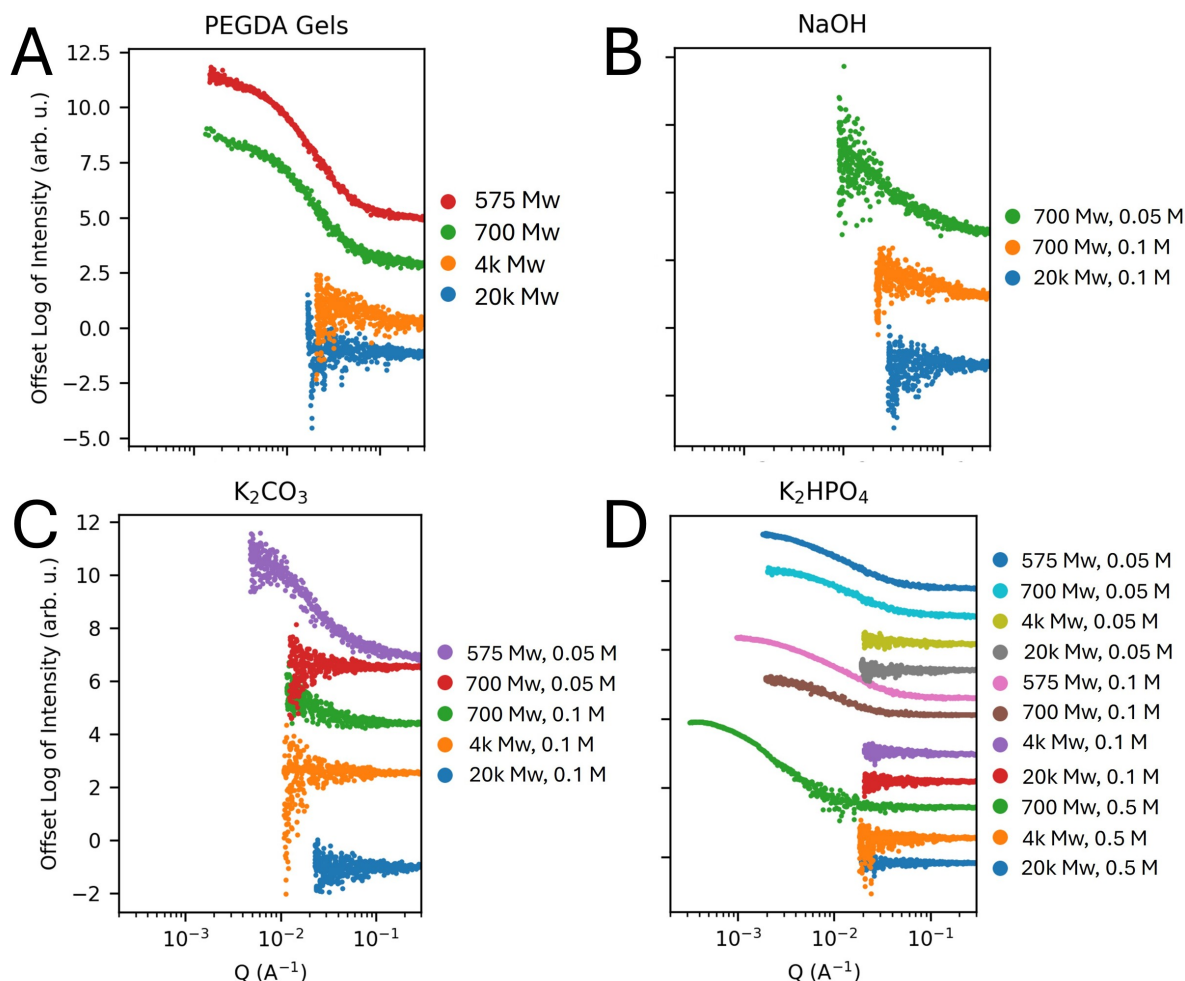


Figure A.5: Ultrasmall angle scattering curves of **A)** PEGDA gels with no added counter ions, **B)** gels of different molecular weights with added concentrations of NaOH, **C)** gels of various molecular weights with added concentrations of K_2CO_3 , and **D)** gels of different molecular weights with added concentrations of K_2HPO_4 . Some gels and counter ion combinations were not measured due to time constraints. USAXS measurements were offset on the y-axis a fixed amount from one another.

(Figure A.7) and 4k PEGDA (Figure A.8, despite the 4k PEGDA having twice the concentration. The sizes of these polydisperse spherical particles tend to shift towards lower q values, indicating larger diameters, towards the bottom of the reaction-diffusion front. This is similar, but less pronounced, compared to the NaOH samples. In many K_2CO_3 samples, the very top of the gel has a different morphology compared to the precipitated particles below it. Increasing the concentration of K_2CO_3 has a predictable trend with respect to the scattering data. When the concentration was 0.05 M K_2CO_3 , the number of scatterers did not produce a significant signal (Figure A.7). The behavior of the 4k PEGDA with 0.1 M K_2CO_3 is also distinct

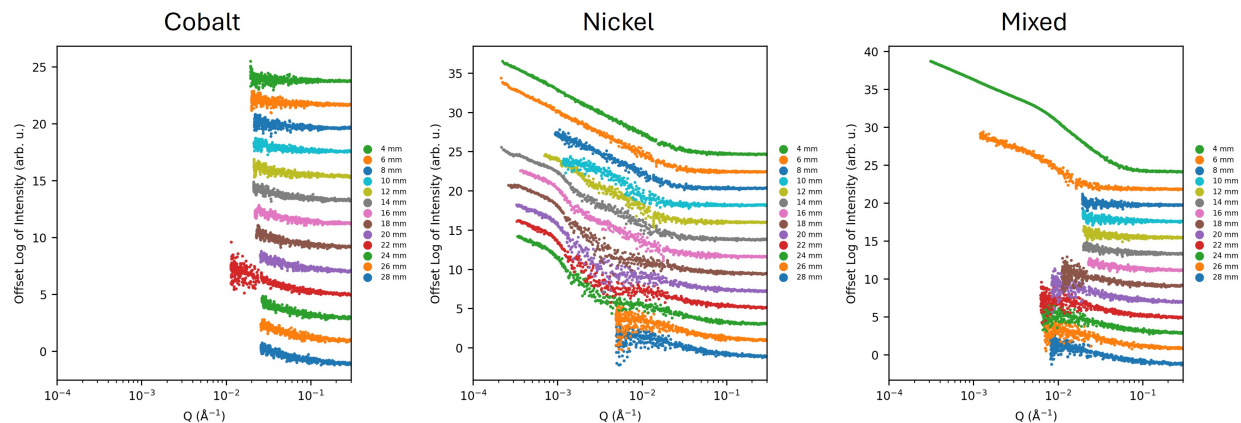


Figure A.6: USAXS curves of 700 molecular weight PEGDA gels prepared with 0.05 M NaOH with outer electrolytes of 5 M CoCl_2 , NiCl_2 , and a 1:1 Ni:Co mix. Measurements were taken from the meniscus of the outer electrolyte (0 mm) to below the bottom of the reaction-diffusion front where outer electrolyte ions had yet to diffuse to. USAXS measurements were offset on the y-axis a fixed amount from one another.

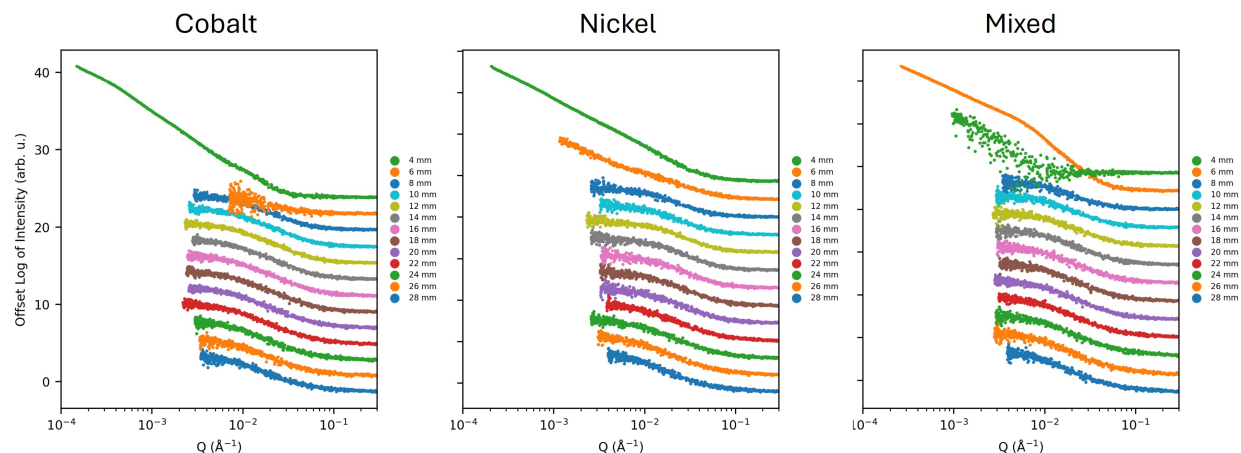


Figure A.7: USAXS curves of 700 molecular weight PEGDA gels prepared with 0.05 M K_2CO_3 with outer electrolytes of 5 M CoCl_2 , NiCl_2 , and a 1:1 Ni:Co mix. Measurements were taken from the meniscus of the outer electrolyte (0 mm) to below the bottom of the reaction-diffusion front where outer electrolyte ions had yet to diffuse to. USAXS measurements were offset on the y-axis a fixed amount from one another.

compared to the 700 PEGDA with an equal concentration of K_2CO_3 . The scattering intensity is again higher than with the lower molecular weight.

It is possible that the difference in behavior between the 700 and 4k PEGDA for the K_2CO_3 reaction-diffusion samples is the gel's structure. PEGDA consists of regions of dense crosslinking diacrylate units surrounded by regions of ethylene glycol chains or water-filled pores.^{2,9} As the molecular weight increases, the crosslinking regions become spaced further apart, and the regions filled with ethylene glycol and water

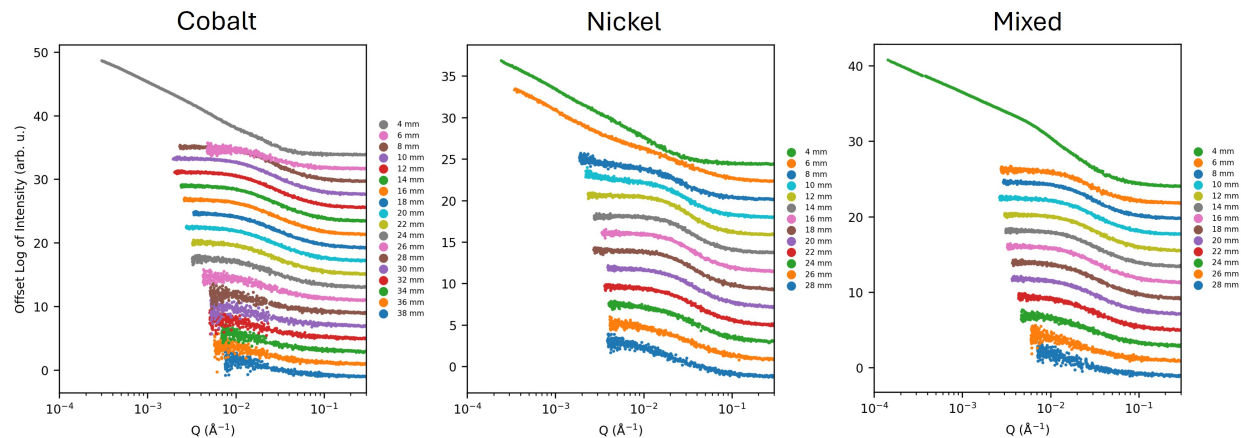


Figure A.8: USAXS curves of 700 molecular weight PEGDA gels prepared with 0.1 M K_2CO_3 with outer electrolytes of 5 M CoCl_2 , NiCl_2 , and a 1:1 Ni:Co mix. Measurements were taken from the meniscus of the outer electrolyte (0 mm) to below the bottom of the reaction-diffusion front where outer electrolyte ions had yet to diffuse to. USAXS measurements were offset on the y-axis a fixed amount from one another.

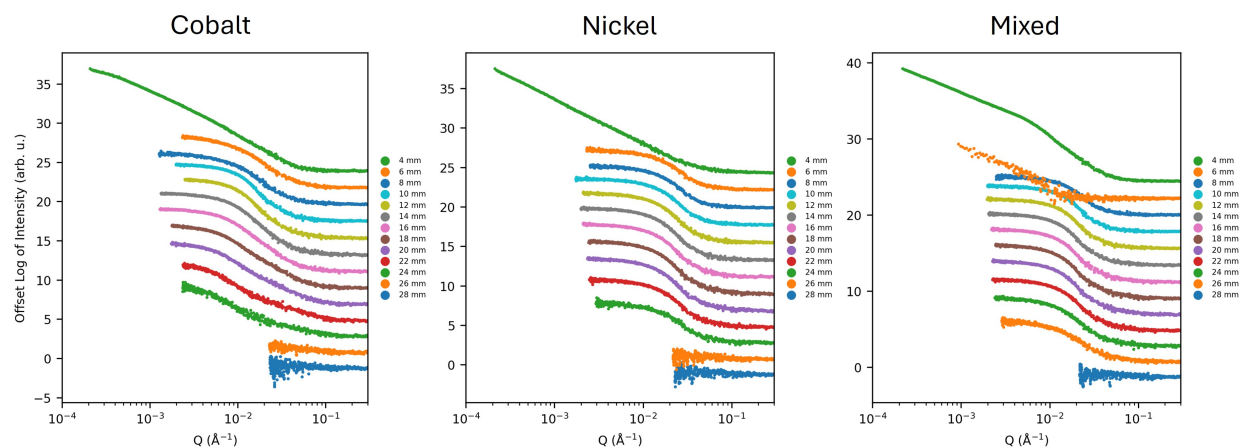


Figure A.9: USAXS curves of 4k molecular weight PEGDA gels prepared with 0.05 M K_2CO_3 with outer electrolytes of 5 M CoCl_2 , NiCl_2 , and a 1:1 Ni:Co mix. Measurements were taken from the meniscus of the outer electrolyte (0 mm) to below the bottom of the reaction-diffusion front where outer electrolyte ions had yet to diffuse to. USAXS measurements were offset on the y-axis a fixed amount from one another.

grow larger. In the longer molecular weight PEGDA, these ethylene glycol regions become bundled and can stretch and deform, giving the gel more elasticity on the macro scale. The shorter PEGDAs are necessarily more rigid as there are more crosslinking centers by mass, making the gel less deformable. In the case where a precipitate is attempting to grow by diffusion of species to the surface, growth may be arrested by the rigid densely crosslinked PEGDA. The particles can grow larger and more numerous in the 4k PEGDA

since there is simply more space. The diacrylate also does a poorer job compared to ethylene glycol chains at solvating hydrophilic species since it is less polar. This may also be a factor. Structurally, the SAXS region also shows a significant difference in the nanostructure of the gel (Figure A.15). Compared to the low intensity pore feature at 3.1 nm in the 575 and 700 gel, a 10 wt% 4k PEGDA has a significant concentration of ~9 nm pores which may significantly affect nucleation. To examine this, gels without a significant nanoporous structure, like agarose or gelatin, can be used to examine the morphology of precipitates in similar experiments.

The crystal structure of CoCO_3 , NiCO_3 , and the 1:1 mixed $\text{Co}^{2+}/\text{Ni}^{2+}$ product were all amorphous (Figure A.10). This is in line with the USAXS measurements, which identified only spherical precipitates without any anisotropy. At the top of the gel in the mixed samples, the crystal phase belonging to a large leaf-shaped platelets is present. This is likely a mixed Co/Ni hydrated chloride phase that settled out of solution an onto the gel.

A.1.3 Simple Reaction-Diffusion Coupling Model in Python

The precipitates formed during reaction-diffusion are largely the products of the concentrations of the reagents over time. To better understand how these dynamic supersaturation conditions can produce the wide range of morphologies we see and, in turn, achieve a deeper level of understanding towards specific crystallization reactions, a robust understanding of the conditions is required. This is where simulation can inform us.

Since the spatial and temporal dimensions within this reaction-diffusion system are related, it is possible to make inferences about the temporal evolution of the precipitates from a snapshot in time of the entire gel column. This is because the concentration profiles over the entire length of the gel after 12 hours or so are similar, but not identical, to the concentration profiles over time at a single point in the gel. The simulated results demonstrate this, as you can essentially take Figure A.11B to be the mirrored reflection of Figure A.11A. In short, at any given point, the outer electrolyte's concentration increases over time as it diffuses inward, in much the same way that its concentration increases spatially from the propagation front up to the top of the gel where the reservoir sits. The biggest dissimilarity is the concentration of the reagents. At the beginning of the reaction-diffusion process, the highly concentrated outer electrolyte reacts with the

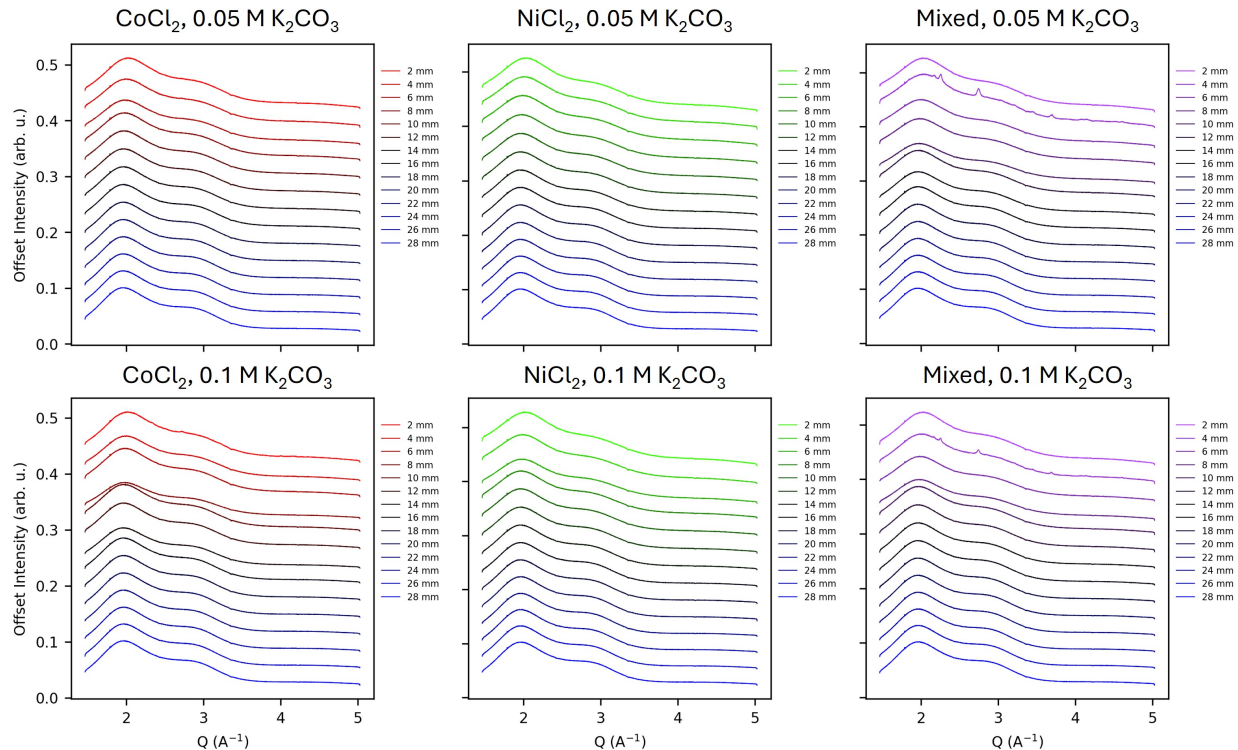


Figure A.10: Wide angle X-ray scattering measurements of reaction-diffusion samples prepared with 4k Mw PEGDA and K_2CO_3 with 5 M aqueous outer electrolytes of $CoCl_2$, $NiCl_2$, and a 1:1 mixture of both $CoCl_2$ and $NiCl_2$. Measurements were taken over the length of the sample from the top of the outer electrolyte (0 mm) to the bottom of the reaction-diffusion front. WAXS measurements were offset on the y-axis a fixed amount from one another.

inner electrolyte before a depletion zone has had the chance to form. After many hours, however, the inner and outer electrolytes are much lower in concentration when they react, as a wider depleted region has developed at the propagation front. Though it should also be noted that the concentration of the reagents has a much smaller impact on the final morphology and crystal structure than the chemistry of the electrolytes. Ultimately the activity matters more for the reaction, not just the concentration.

Simulation Details

To model the reaction-diffusion process inside the gel, we utilize the 1D diffusion equation (Equation 5.4) where D_i is the molecular diffusivity of the cobalt and phosphate species. We assume an irreversible reaction of the form $3 Co^{2+} + 2 PO_4^{3-} \longrightarrow CO_3(PO_4)_2$ with a reaction term of $r = kC_{Co}^3C_{PO_4}^2$. A very fast nucleation and reaction rate, due to the low solubility (2.05×10^{-35}),¹⁰ makes the system of equations very

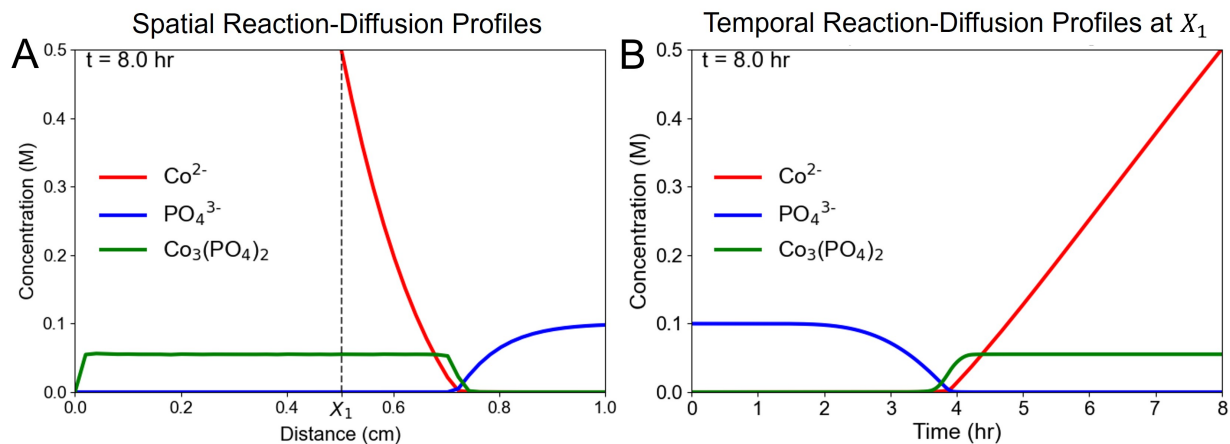
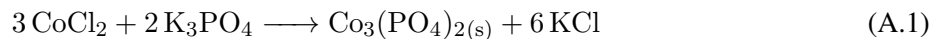


Figure A.11: Simulated reaction-diffusion concentration profiles in a 1D system over **A)** the entire simulated space and **B)** all time at a single position, X_1 , indicated by a dotted line in spatial plot.

stiff. No difference in the final modeled effective diffusivity of the propagation front was seen when the reaction rate constant, k , was above $10^6 \text{ M}^{-4} \text{ s}^{-1}$ so a rate constant of $10^8 \text{ M}^{-4} \text{ s}^{-1}$ was chosen for stability. The effect that a faster reaction rate has is to 'sharpen' the propagation front.¹¹ An extremely sharp transition between the solid cobalt(II) phosphate precipitate and the clear gel in Figure 5.1B demonstrates this sharp front. The system was modeled with Neumann boundary conditions (zero flux) at the edges of the simulation ($x = 0$ and $x = L$) and the following initial conditions for the 10 cm length: $C_{\text{Co}}(t = 0, x \leq 1) = 5 \text{ M}$ and $C_{\text{PO}_4}(t = 0, x > 1) = 0.1 \text{ M}$. Molecular diffusivities were taken from literature ($D_{\text{CoCl}_2} = 1.86 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $D_{\text{K}_2\text{HPO}_4} = 1.11 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).^{12,13} These molecular diffusivities are accurate only when considering extremely dilute conditions in water at room temperature. These are inaccurate for the simulated system as they don't account for the relatively high concentrations and the interaction with the gel medium. We assume the precipitate's diffusion is zero in the gel. Within the simulation, the position of the propagation front at each timestep of the simulation was tracked *via* a 10% threshold of the max concentration. As the concentration increased above the threshold, it created a traveling wave that was fit with the same mean-square-displacement as the measured reaction-diffusion experiments.

Governing Equations

The system models the irreversible precipitation reaction:



Partial Differential Equations

$$\frac{\partial[\text{Co}]}{\partial t} = D_{\text{Co}} \frac{\partial^2[\text{Co}]}{\partial x^2} - 3r \quad (\text{A.2})$$

$$\frac{\partial[\text{PO}_4]}{\partial t} = D_{\text{PO}_4} \frac{\partial^2[\text{PO}_4]}{\partial x^2} - 2r \quad (\text{A.3})$$

$$\frac{\partial[\text{Solid}]}{\partial t} = D_{\text{solid}} \frac{\partial^2[\text{Solid}]}{\partial x^2} + r \quad (\text{A.4})$$

Reaction rate

$$r = k[\text{Co}]^3[\text{PO}_4]^2 \quad (\text{A.5})$$

where $k = 10^8 \text{ M}^{-4}\text{s}^{-1}$ is the reaction rate constant

Boundary Conditions

All species obey Neumann (zero-flux) boundary conditions at both boundaries.

At $x = 0$ (left boundary):

$$\left. \frac{\partial[\text{Co}]}{\partial x} \right|_{x=0} = 0, \quad \left. \frac{\partial[\text{PO}_4]}{\partial x} \right|_{x=0} = 0, \quad \left. \frac{\partial[\text{Solid}]}{\partial x} \right|_{x=0} = 0 \quad (\text{A.6})$$

At $x = L$ (right boundary):

$$\left. \frac{\partial[\text{Co}]}{\partial x} \right|_{x=L} = 0, \quad \left. \frac{\partial[\text{PO}_4]}{\partial x} \right|_{x=L} = 0, \quad \left. \frac{\partial[\text{Solid}]}{\partial x} \right|_{x=L} = 0 \quad (\text{A.7})$$

Code

```
1 import numpy as np
2 from scipy.integrate import solve_ivp
```

```

3  import matplotlib.pyplot as plt
4  # --- spatial grid ---
5  L = 5
6  N = 250
7  x = np.linspace(0, L, N)
8  dx = x[1] - x[0]
9  # --- parameters ---
10 D_Co = 1.086e-6      # Molecular diffusion coefficient for Co
    ↪ https://pubs.acs.org/doi/10.1021/je0101808
11 D_PO4 = 1.11e-6     # Diffusion coefficient for PO4
    ↪ https://doi.org/10.3390/liquids3030018
12 D_solid = 0.0        # solid doesn't diffuse in gel
13 k = 1e8              # reaction rate constant
14 t_span = (0, 8*3600) # 8 hours
15 t_eval = np.linspace(*t_span, 1000)
16 # --- initial conditions ---
17 Co0 = np.zeros(N)
18 PO40 = np.zeros(N)
19 Solid0 = np.zeros(N)
20 # Cobalt Concentration
21 Co0[: N // 250] = 5 # Assumes the cobalt starts inside the gel
22 # PO4 Concentration
23 PO40[N // 250 :] = 0.1 # Assumes the rest of the space is filled with
    ↪ phosphate
24 # concatenate into single vector
25 C0 = np.concatenate([Co0, PO40, Solid0])
26 # --- helper: 1D Laplacian with zero-flux BCs ---
27 def laplacian(u):
28     dux2 = np.zeros_like(u)
29     dux2[1:-1] = (u[2:] - 2 * u[1:-1] + u[:-2]) / dx**2
30     return dux2
31 # --- PDE system ---

```

```

32 def rhs(t, C):
33     Co = C[0:N]
34     PO4 = C[N:2*N]
35     Solid = C[2*N:3*N]
36     # Reaction rate (irreversible)
37     r = k * (np.maximum(Co, 0)**3) * (np.maximum(PO4, 0)**2)
38     d2Co = laplacian(Co)
39     d2PO4 = laplacian(PO4)
40     d2Solid = laplacian(Solid)
41     dCo_dt = D_Co * d2Co - 3 * r
42     dPO4_dt = D_PO4 * d2PO4 - 2 * r
43     dSolid_dt = D_solid * d2Solid + r
44     return np.concatenate([dCo_dt, dPO4_dt, dSolid_dt])
45 # --- solve the system ---
46 sol = solve_ivp(rhs, t_span, C0, t_eval=t_eval, method="Radau")
47 # --- extract concentrations ---
48 Co_sol = sol.y[0:N, :]
49 PO4_sol = sol.y[N:2*N, :]
50 Solid_sol = sol.y[2*N:3*N, :]

```

A.1.4 References

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A.2 Characterizing Hydrogels with SAXS

Reaction-diffusion coupling in hydrogels is dependent upon a host of factors. The chemistry and subsequent structure of the hydrogel are central to this laundry list of parameters. We identify through SAXS that keeping the inner electrolyte concentration below 0.1 M results in very little change in the structure of the gel in most cases. The weight fraction of the gel, and the concentration of any crosslinkers, had a much larger effect on the structure, as can be seen in Figure A.15 for PEGDA and Figure A.12 for polyacrylamide. In some cases the hydrogels would not gel properly and would instead flow when their container was inverted after curing. This was more common with longer PEGDA polymers like 4k and 20k when using a lower weight percent or when a high amount of the more caustic counter ions like K_3PO_4 were added. Generally, when the weight percent of the gel was 10wt% and the concentration of the counter ion was at or below 0.1 M, proper gelling occurred in all samples with minimal disruption to the gel structure compared to the gel without ions. This was the standard parameters used for most reaction-diffusion experiments for this reason.

When it comes to preparing the hydrogel, some counter ions affect the crosslinking and formation of the 3D network, depending on the compatibility between the gel and the ion. For the PEGDA hydrogels we investigated (575, 700, 4k, and 20k g/mol), the 4k and 20k Mw hydrogels struggled to gel completely when higher concentrations of a counter ion were added. NaOH prevented gelation at concentrations around 0.5 M for every PEGDA, while with K_2HPO_4 gelation still occurred at 0.5 M or below. For shorter polymers, such as PEGDA with molecular weights of 575 and 700 g/mol, at higher concentrations of K_2HPO_4 the gel became an opaque white, indicating structural inhomogeneities in the gel that scatter strongly in the visible spectrum.¹ Polyacrylamide and agarose were much more stable when a counter ion was added. When the gels were prepared with 0.1 M K_2HPO_4 or NaOH, only small differences in the X-ray scattering were observed, indicating little structural change. No change in color or structure was observed until 0.5 M of a counter ion was added.

A.2.1 Polyacrylamide

Polyacrylamide is prepared using the acrylamide monomer and a crosslinker, which in these experiments was N,N'-methylenebis(acrylamide) (Baam). The total weight fraction (wt% T) is the mass fraction of both the acrylamide monomer and the Baam monomer. The percentage of crosslinker (%C) is the percentage of Baam with respect to the total mass of acrylamide and Baam. The equations below define the percentages,

where m_A is the mass of the acrylamide monomer, m_C is the mass of the crosslinker, m_T is the total mass of the sample, m_L is the mass of the photoinitiator, m_k is the mass of the counter ion, and m_w is the mass of water. The molarity of the counter ion, M_k , is calculated based on the mass of water in solution using the molecular weight of the counter ion, MW_k .

$$T(\text{wt}\%) = 100 \frac{m_A + m_C}{m_T} \quad (\text{A.8})$$

$$C(\%) = 100 \frac{m_C}{m_A + m_C} \quad (\text{A.9})$$

$$L(\%) = 100 \frac{m_L}{m_T} \quad (\text{A.10})$$

$$m_T = m_A + m_C + m_w + m_k + m_L \quad (\text{A.11})$$

$$M_k = 1000 \frac{m_k}{MW_k m_w} \quad (\text{A.12})$$

Polyacrylamide was shown to be the most resistant to the addition of an inner electrolyte. When K_2HPO_4 was added to 10, 15, and 20 wt% T polyacrylamide, the scattering curve changed only marginally, and only once the concentration of K_2HPO_4 reached 0.5 M (Figure A.12). Increasing the weight fraction of monomer did not affect the extent to which the K_2HPO_4 altered the gel. The scattering profiles of the 10 and 15 wt% T polyacrylamide gels had a constant power law slope of -1.52 in the Porod region, which is expected for a polymerized gel with semi-stiff polymer chains.² These results demonstrated that the structure of the gel was largely unaffected in the weight fraction range from 10 to 20 wt% T for K_2HPO_4 concentrations at or below 0.1 M.

The effect of the crosslinking concentration was also measured with respect to various inner electrolytes (Figure A.13). A higher percentage of crosslinking units (% C) is correlated with larger domains within the polyacrylamide hydrogel.³ With a crosslinker percentage of 10%, the polyacrylamide's SAXS curves are relatively featureless aside from a change in the power law slope at approximately $0.05 \text{ \AA}^{-1}$, with the low-Q

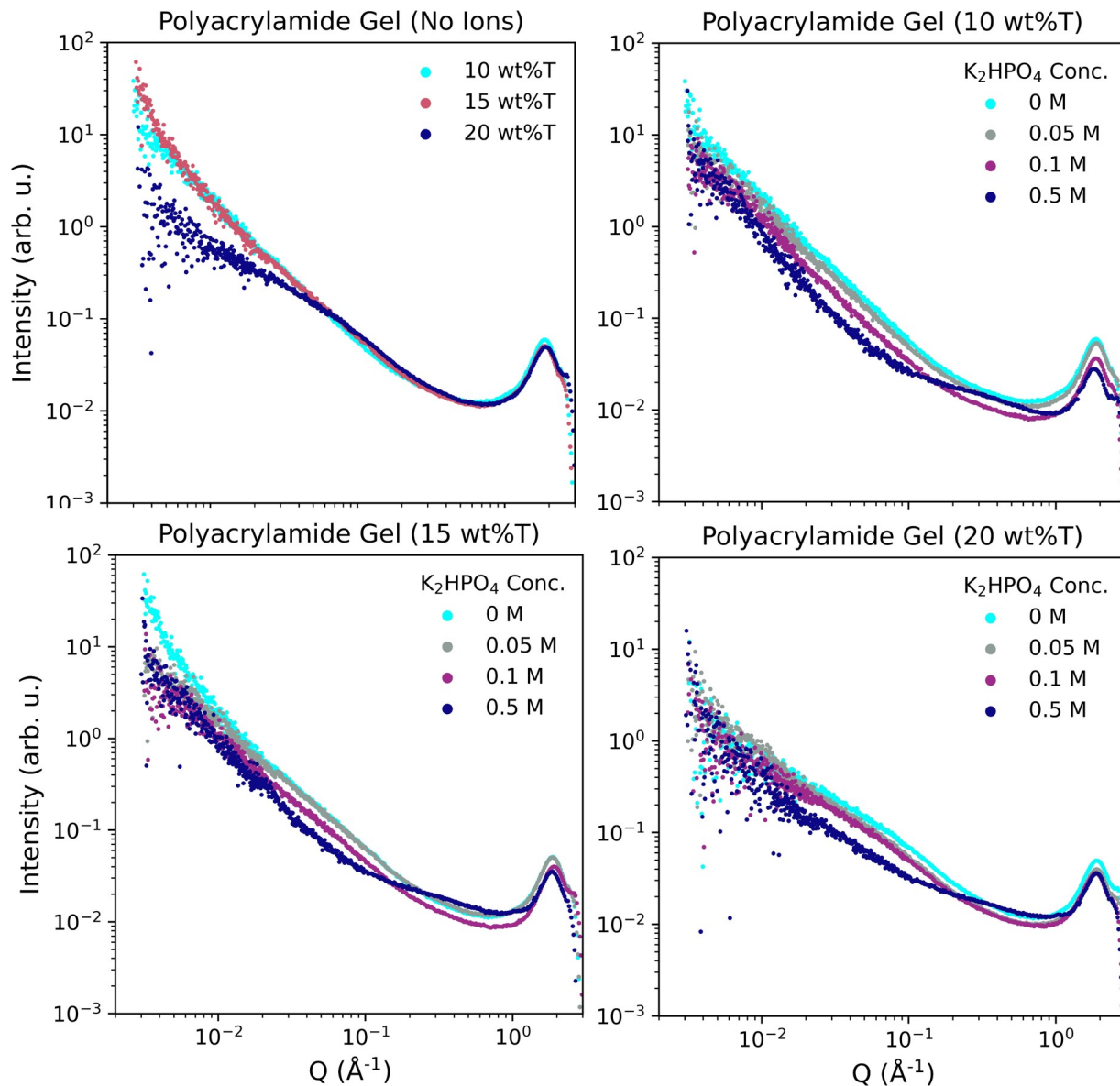


Figure A.12: Merged SAXS/WAXS curves of polyacrylamide hydrogels (5% crosslinker) with **A)** different weight percents between 10 and 20 wt% total monomer. Increasing K_2HPO_4 concentrations from 0 to 0.5 M show very little change in the structure for different weight fractions of polyacrylamide, including **B)** 10 wt% T, **C)** 15 wt% T, **D)** and 20 wt% T.

region having a power law slope of -2.5 that becomes -1.7 between 0.05 and $1 \text{ \AA}^{-1}$ (10 wt% T, 10%C). Decreasing the crosslinker percentage to 5%, the overall scattering at low q decreases indicating smaller domains. The power law slope of the scattering curve also decreases to -1.39 (10 wt% T, 5%C). This is consistent with the polyacrylamide becoming more flexible as the amount of crosslinker is decreased.²

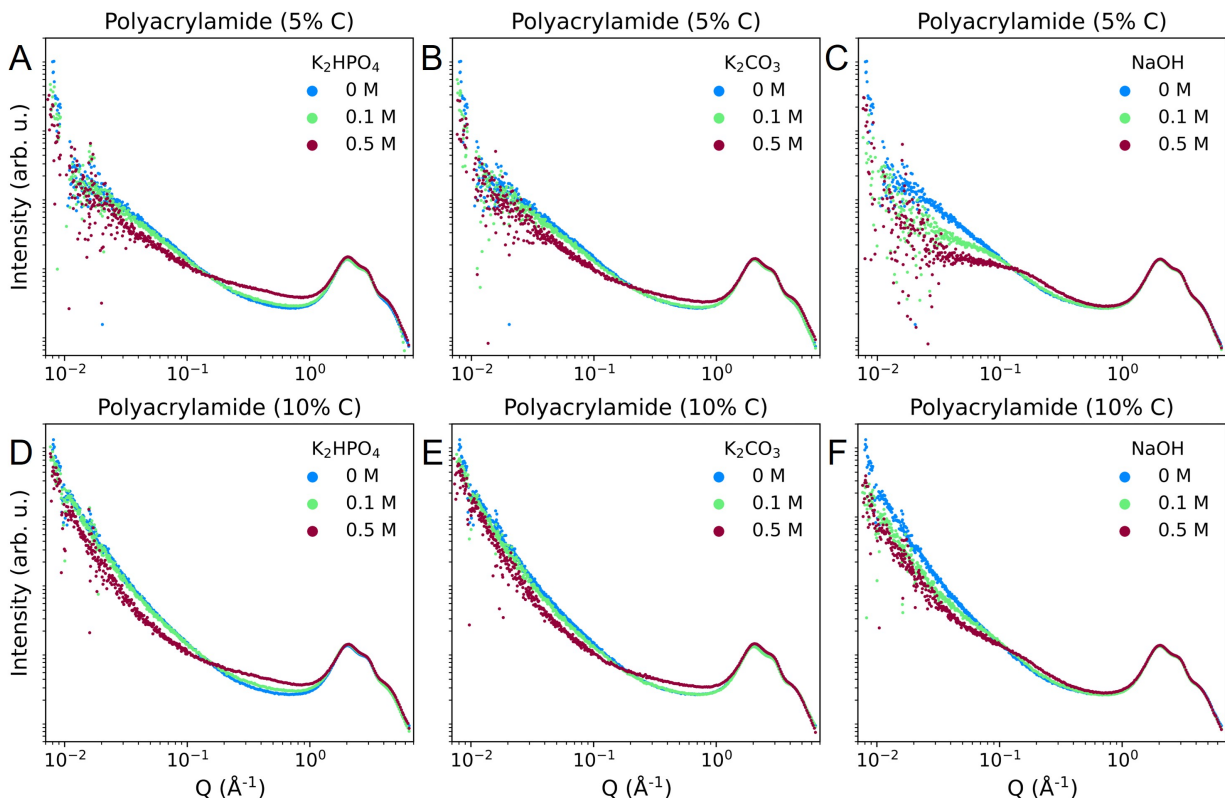


Figure A.13: Merged SAXS/WAXS curves of polyacrylamide hydrogels, all with a total monomer concentration of 10 wt%, with 5 and 10% crosslinker. One set of gels was prepared with 5% crosslinker and 0, 0.1, and 0.5 M of **A)** K_2HPO_4 , **B)** K_2CO_3 , and **C)** NaOH . The second set was prepared with 10% crosslinker and 0, 0.1, and 0.5 M of the same electrolytes **D)** K_2HPO_4 , **E)** K_2CO_3 , and **F)** NaOH .

With respect to the inner electrolytes K_2HPO_4 , K_2CO_3 , and NaOH , the electrolyte with the largest effect on the structure was NaOH . Figure A.13C shows that when the crosslinking concentration was 5 %C, the NaOH disrupted the larger domains in the gel as evidenced by the decreasing scattering intensity at low- Q . There was a less dramatic effect when the crosslinker concentration was 10%C (Figure A.13F), but it was still noticeable compared to K_2HPO_4 and K_2CO_3 , which resulted in no change to the scattering domains until 0.5 M. These results further verified that below 0.1 M the inner electrolyte has very little effect on the structure of the gel regardless of crosslinking concentration, with the noted exception of NaOH . The effect of some counter ions on the structure after changing both weight fraction and percent crosslinker was also measured, which demonstrated that at 0.1 M, K_2HPO_4 and K_3PO_4 had little effect on the structure (Figure A.14).

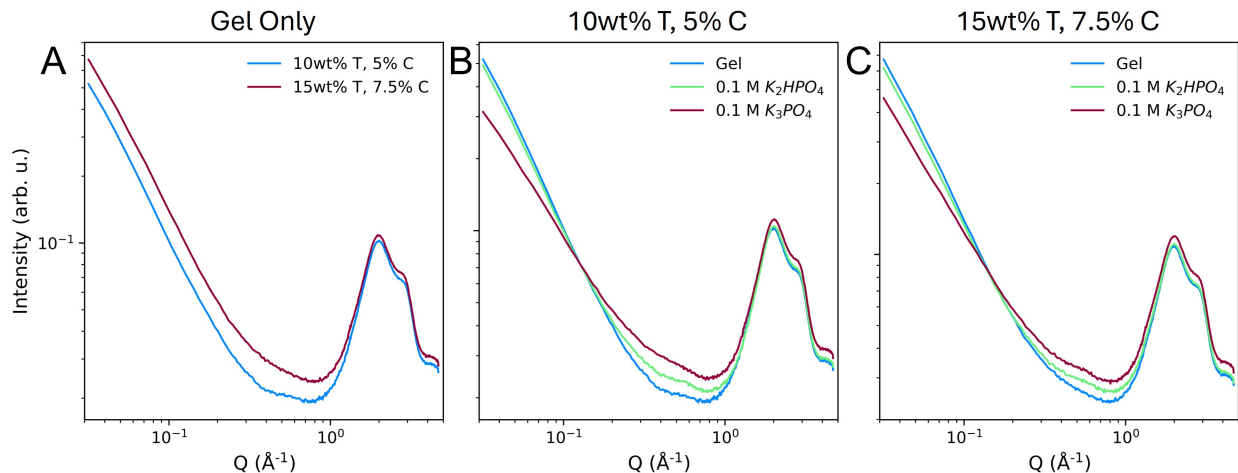


Figure A.14: **A)** Comparison of SAXS/WAXS measurements on polyacrylamide gels without counter ions prepared at 10 wt% (5%C) and 15 wt% (7.5%C). **B)** The 10 wt%, 5%C gel compared to identical gels prepared with 0.1 M K_2HPO_4 and K_3PO_4 . **C)** The 15 wt%, 5%C gel compared to identical gels prepared with 0.1 M K_2HPO_4 and K_3PO_4 .

A.2.2 Polyethylene glycol diacrylate

Preparing reaction-diffusion samples with polyethylene glycol diacrylate (PEGDA) is simpler than with polyacrylamide since no separate crosslinker is added. Similar to the polyacrylamide mass and molar fraction calculations (Equation A.8–Equation A.12), the molarity (technically molality, since we assume a density of 1 g/mL for water) is calculated based on the mass of water, not the mass of the water plus the mass of the gel.

The structure of the PEGDA after gelling is dependent on the molecular weight of the PEGDA as well as the weight fraction of the gel in solution. The weight fraction for 700 g/mol PEGDA was adjusted between 2 and 50 wt%, and a scattering profile was measured (Figure A.15A). This covers the full range of the structure of the gel, from 2 and 5 wt%, which are insufficient in concentration to hold the shape of the container, to 50wt%, which is tough and brittle. In these samples, a feature around $0.2 \text{ \AA}^{-1}$ ($d = 3.1 \text{ nm}$) can be seen, which is attributed to a bottle-brush-like structure around the diacrylate groups that develops during polymerization.⁴ This feature is primarily associated with the molecular weight of the PEGDA polymers, which is why changing the weight fraction of the 700 gel in Figure A.15A has little effect on the feature's position. This indicates that the feature size is independent of weight percent. There are, however, more significant changes between samples at lower Q , corresponding to length scales of 10 to 300 nm. These

are likely the result of changes to larger domains within the gel that are areas of higher polymer density.⁵ Both the highest and lowest weight fractions have very similar scattering profiles that are lower in intensity than those of the other weight fractions. This indicates that the two are more uniform, with fewer of these domains to scatter the beam.

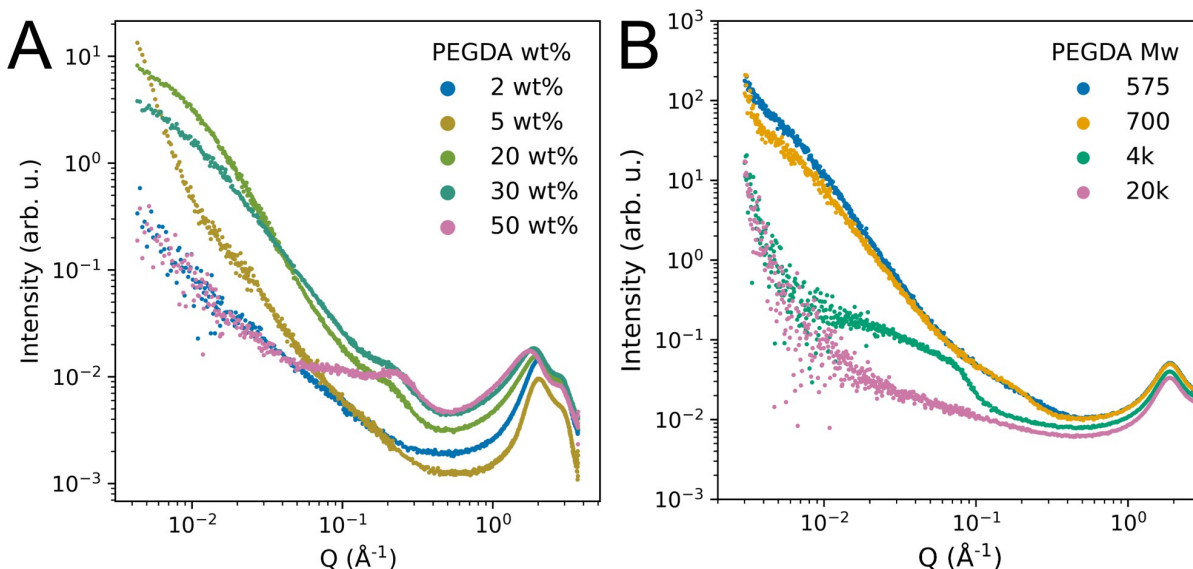


Figure A.15: **A)** Small angle X-ray scattering curves of 700 Mw PEGDA at a range of weight percents without counter ions. **B)** Small angle X-ray scattering curves of various molecular weights of 10 wt% PEGDA identified in g/mol.

There are also significant changes in the gel structure when the molecular weight is changed (Figure A.15B). There is little difference between the 575 and 700 g/mol gels, as expected, but there are significant differences between the 700, 4k, and 20k g/mol PEGDAs. The 4k PEGDA has a large feature at $0.07 \text{ \AA}^{-1}$ in q -space ($d = 9.0 \text{ nm}$). A feature of this size is also likely to arise from the nanopores formed during diacrylate polymerization. The 20k PEGDA is missing this feature either because it is large enough to fall outside the measurable Q -range of the Xenocs Xeuss 3.0, or because the scattering of the Kapton window in the sample holder overlaps significantly.

The reaction-diffusion experiments require that the PEGDA be sufficiently polymerized to form a 3D network, meaning that the gel must hold the shape of the container unsupported to prevent immediate mixing of the outer electrolyte with the counter ion. This is true of every hydrogel, but among PEGDA, agarose, and polyacrylamide, PEGDA is the most susceptible to incomplete gelation. Gelation can be assessed quickly by

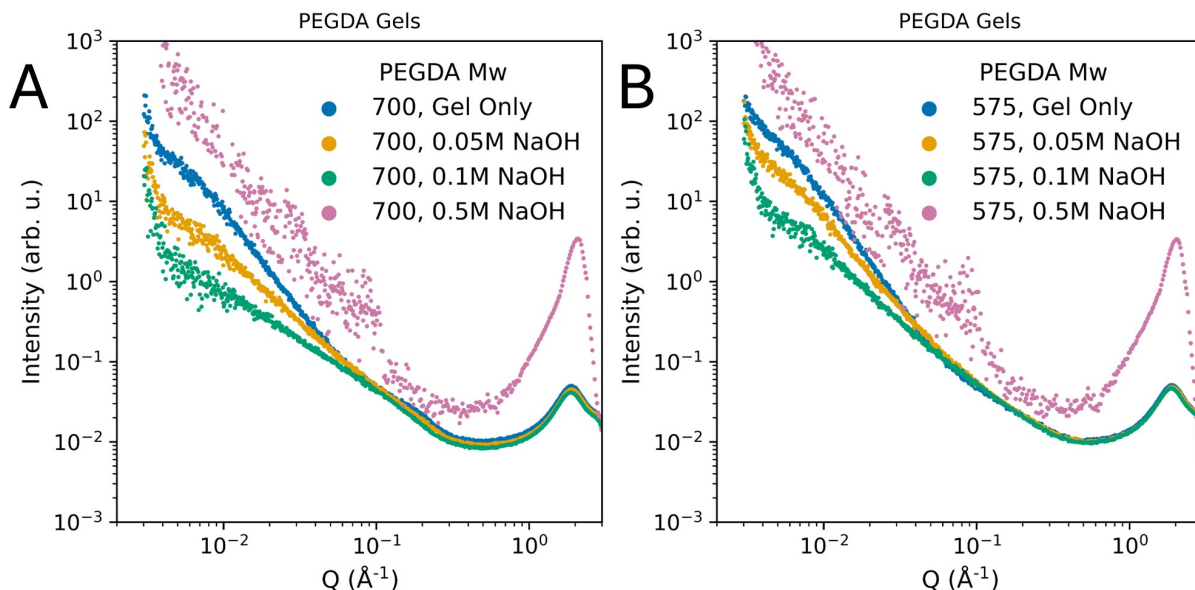


Figure A.16: A) SAXS curves of 575 g/mol PEGDA prepared with 0.05 and 0.1 M NaOH. B) SAXS curves of 700 g/mol PEGDA prepared with 0.05 and 0.1 M NaOH.

inverting a container of the PEGDA and counter-ion solution after UV curing and if there is flow, then it is not fully gelled. It is possible that flow can also occur if the weight fraction of the PEGDA is so low that the 3D network does not properly form, which was an issue for most molecular weights below approximately 7 wt%. The identity and concentration of the counter ion also influenced this, with two of the counter ions in this work, NaOH and K_2CO_3 , negatively impacting the gelation process. Lower molecular weights of PEGDA gelled more easily, even with higher concentrations of these counter ions. With 10 wt% PEGDA, NaOH was the most detrimental, preventing every PEGDA (575 through 20k g/mol) from gelling at 0.5 M and preventing the longer PEGDAs (4k and 20k) from gelling above even 0.1 M. In Figure A.16, the shorter PEGDAs (575, 700 g/mol) that had a NaOH counter ion were measured by SAXS. The gels with 0.5 M NaOH were unable to gel.

The SAXS curves in Figure A.17 and Figure A.18 show the changes in structure for the K_2CO_3 and K_2HPO_4 counter ions used in some experiments. They show that in the carbonate and phosphate cases below 0.5 M, the structure is largely unaffected, which indicates polymerization is unaffected by the presence of these counter ions. The two features at higher Q , around 1 and 2 $\text{\AA}^{-1}$, are due to water, which is predominantly responsible for the scattering because it has a higher SLD than PEGDA. In samples with

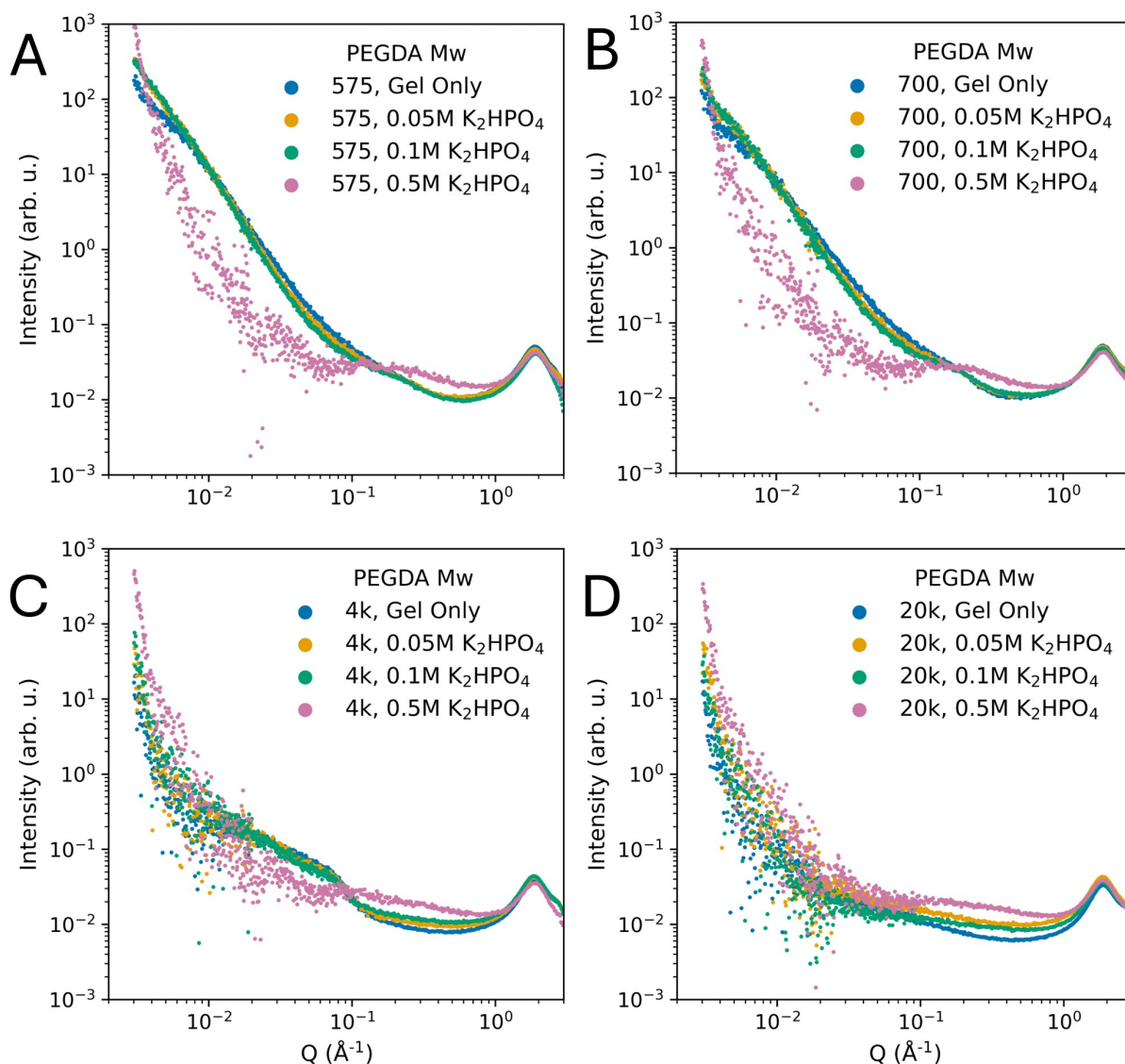


Figure A.17: SAXS curves of samples prepared with 0.05, 0.1, and 0.5 M of K_2HPO_4 in **A)** 575, **B)** 700, **C)** 4k, and **D)** 20k g/mol PEGDA.

larger amounts of K_2CO_3 or K_2HPO_4 (0.1 M or higher), the gel becomes an opaque white. This is due to the electrolyte disrupting the gel in such a way that structural changes within it begin scattering light in the visible spectrum.¹

SAXS using a lab-scale instrument and a sample holder with Kapton windows is better suited to measuring the structure of these gels than USAXS at the APS is. The Bonse-Hart configuration at APS has higher background scattering noise, and because SAXS was not available for most experiments, the data collected

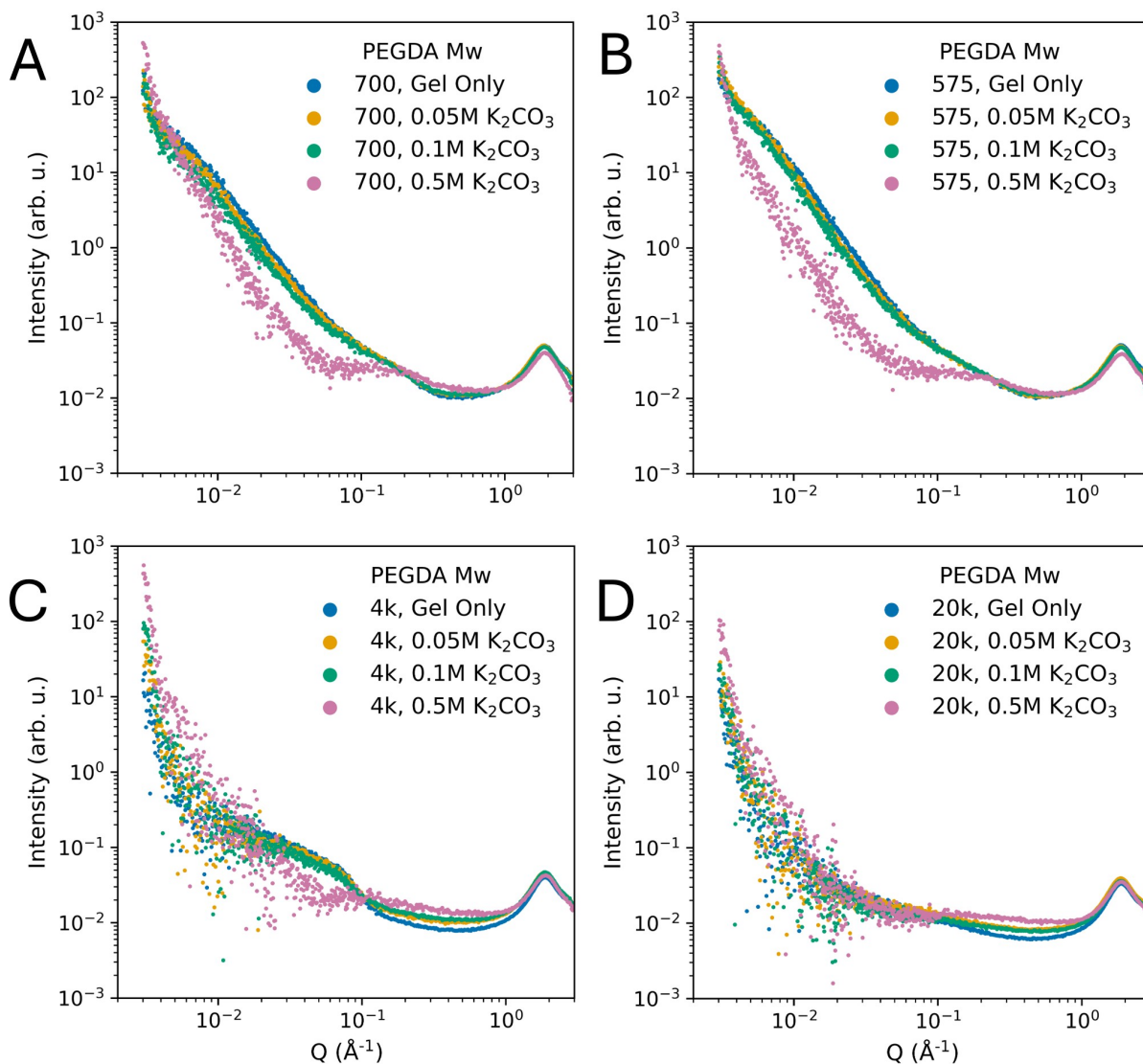


Figure A.18: SAXS curves of samples prepared with 0.05, 0.1, and 0.5 M of K_2CO_3 in A) 575, B) 700, C) 4k, D) 20k g/mol PEGDA.

falls outside the relevant size range. It is, however, useful data to collect as a comparison. USAXS curves of the samples prepared with NaOH and K_2CO_3 show there is a significant change in the scattering profile's intensity for the lower molecular weight samples, while no change is discernible for the higher molecular weights in the USAXS regime. Significant structural changes were seen in SAXS for the 700 Mw PEGDA as well, but as previously stated, no change in the nanopores brought on by the polymerization could be identified. This structural change could be caused by a number of factors, such as a collapse of the macro-

pores, or a greater dispersity of macropore effective radii. Given that the morphologies of the precipitates in this study are more significantly affected by the type of gel and the chemistry of the inner electrolyte, the structure of the gel itself is likely unimportant to the final morphology compared to these other factors.

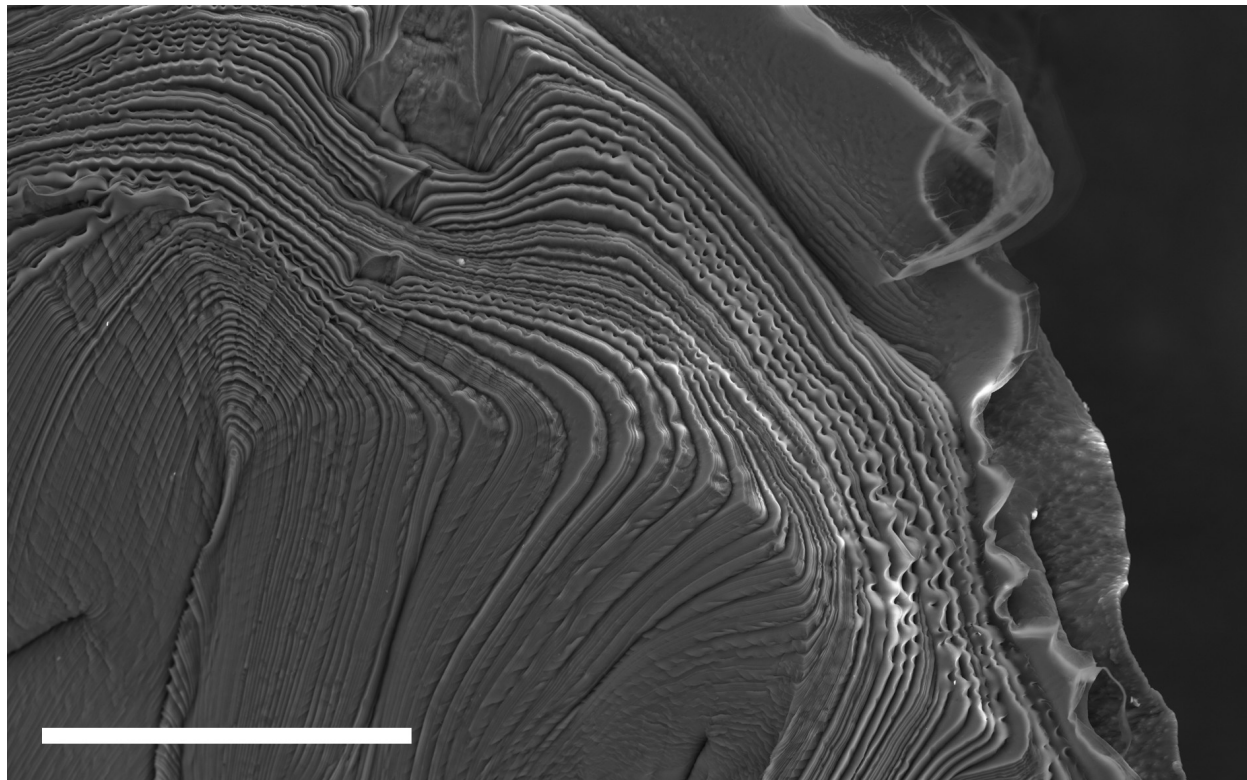


Figure A.19: Scanning electron microscopy image of a dried PEGDA hydrogel (20k Mw, 10 wt%) without any added counter ion. Scale bar (white) is 200 μm .

SAXS is a very useful tool for determining changes in structure, but SEM is required to determine rough chemical compositions and confirm particle morphologies. SEM images of the dried 20k PEGDA without any counter ions (Figure A.19) and with 0.5 M potassium phosphate (Figure A.20) are included. Since the gel has been dried, a significant amount of crystallized counter ion is present both on and below the surface of the gel. It is possible to partially wash away the surface crystals, but as the gel dries, the counter ions continue to work their way to the surface, making repeated washes necessary. SEM-EDS (Figure A.20C–F) and the EDS spectra (Figure A.20B) easily distinguish the potassium phosphate crystals from the surrounding gel which makes slow, repeated washes difficult to justify given the diminishing returns.

In Figure A.20, two morphologies of potassium phosphate crystals present in the sample: large deposits

on the surface, and smaller crystals below the surface. The crystals likely result from the drying procedure as the potassium phosphate transports to the surface and nucleates within the gel as the concentration increases during evaporation.

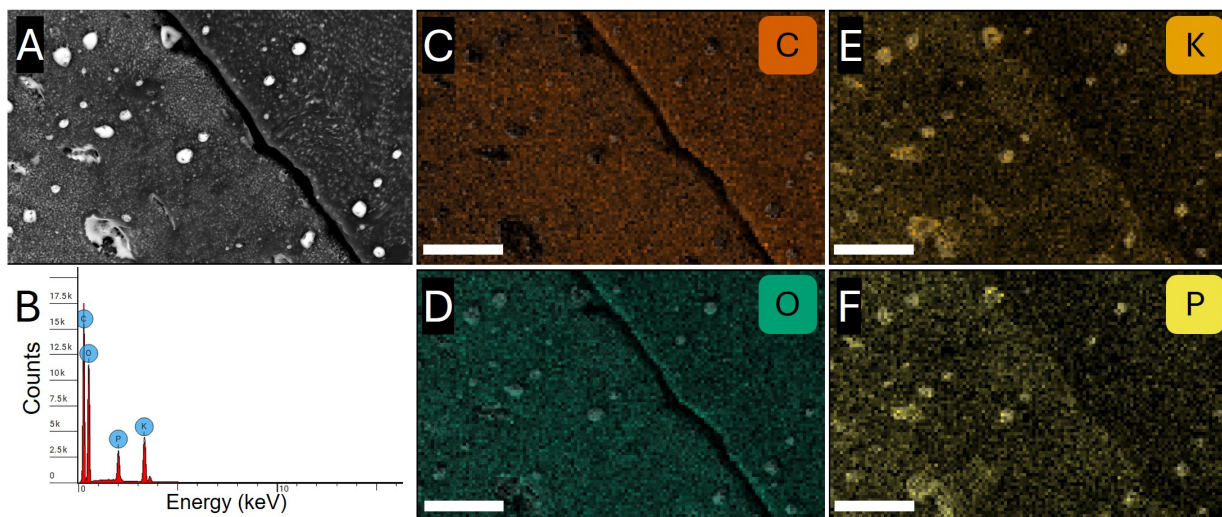


Figure A.20: **A)** Scanning electron microscopy image of a dried PEGDA hydrogel (20k Mw, 10 wt%) prepared to have 0.5 M K_2HPO_4 . **B)** The energy dispersive spectra along with maps of the **C)** carbon, **D)** oxygen, **E)** potassium, **F)** and phosphorus. Scale bar (white) is 30 μm (3300x Mag, accelerating voltage of 20 kV).

A.2.3 References

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