FABRICATION AND PURIFICATION OF SELF-MOTILE NOBLE METAL-SEMICONDUCTOR ACTIVE COLLOIDAL DEVICES

A Dissertation in
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by
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COLLOIDAL ASSEMBLY IS A FIELD OF SCIENTIFIC RESEARCH THAT CAN BE FOUND AT THE INTERSECTION OF MANY FIELDS AND DISCIPLINES. AS A RESULT, CHEMISTS, PHYSICISTS, MATERIALS SCIENTISTS, AND CHEMICAL ENGINEERS ARE ALL ACTIVE IN ASSEMBLY RESEARCH. HOWEVER, MOST ASSEMBLIES CURRENTLY BEING FABRICATED ARE OF MODEL SYSTEMS (SUCH AS ASSEMBLIES OF INERT POLYMER MICROPARTICLES) AND ARE ASSEMBLED USING MATERIAL-SPECIFIC TECHNIQUES THAT PRODUCE ONLY LAB SCALE QUANTITIES OF PRODUCT.


THE FUNCTIONAL COLLOIDAL ASSEMBLY PRODUCED HERE IS A THREE-COMPONENT COLLOIDAL ‘TRIMER’ CONSISTING OF THREE MICRON-SIZED PARTICLES ATTACHED IN A SPECIFIC ORDER, I.E., GOLD – CADMIUM SULFIDE – SILVER, BUT WITHOUT A SPECIFIC ORIENTATION. THE ASSEMBLY PROCESS USED TO FORM THESE TRIMERS IS DEVELOPED AND CHARACTERIZED IN THIS WORK. IT IS A DIFFUSION-LIMITED, SELECTIVE, CONTROLLED AGGREGATION PROCESS CALLED ‘QUENCHED ELECTROSTATIC ASSEMBLY’.

Because colloidal assembly is such a broad field, this work encompasses many different fields: interparticle forces, diffusion and aggregation kinetics, catalysis, photoelectrochemistry, geology, and solution electrodynamics, along with many types of colloidal functionalization and analysis.
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I think in my heart I always knew I’d end up at Penn State. That’s what happens when you’re born and raised Blue and White. My father, having grown up in Clearfield just 45 minutes west of State College, got both his Bachelors and his Masters degrees here, and even after he moved to Pittsburgh he made nearly every home game when I was growing up. At least once a season, he’d take me with him. We’d stay with my grandparents on Friday night, then wake up early on Saturday and join the caravan of cars trekking east along Rt 322, backed up for miles, from the Stadium Lot to Port Matilda. I wasn’t the biggest football fan when I was younger, but I knew that those games I attended were something special. Penn State was something special.

Even as I proudly and arbitrarily announced to my parents in middle school that I was going to Carnegie Mellon (which I somehow managed to accomplish several years later), a little voice in the back of my head told me that I would find my way back to State College eventually. I remember attending the 2005 Ohio State game with my dad, cousin, and college roommate. At that point, I was still unsure if graduate school was the right place for me. After that game, I knew that if any grad school was indeed a part of my future, it was Penn State. And so here I am.

I’m happy to say, almost 6 years later, that Penn State was absolutely the right place for me, even if it was for reasons completely different than the ones running through my head as a college senior. I may have been entranced by the football community back then, but I leave here knowing it is the scientific community that made these past 5 years so special. That community, really more of a family for me, is naturally based around my lab group. Their friendship, support, and collaboration have made me into the scientist – and person – that I am today, and for that they have my heartfelt thanks.
I’ll start by thanking the senior lab members, Dr. Allison Yake and Dr. Charles Snyder, who always made the time and effort to be a mentor to the three incoming first-year students Darrell heaped on them as they were trying to graduate. I now understand how difficult it can be to be active in the lab during such a frantic time. Dr. Huda Jerri always pushed me to be a better grad student and scientist (even when it was out of spite), and our long list of mostly unsuccessful collaborations managed to eventually bear fruit: without her, calcium carbonate would have never entered the lab. Each one of my fellow students and collaborators, Dr. Neetu Chaturvedi, Dr. Li-Ju Wang, Cesar Gonzalez Serrano, Laura Mely Ramirez, and Tso-Yi Chiang have all made a big impact on the work that I have done. The work I present in this dissertation is stitched together from the fabric of a thousand conversations and ideas gained by their presence, and I must thank them all for that. I’ve also been blessed with so many excellent undergraduate researchers and collaborators: Erin, Chris, Dave, Kristin, Majd, Steve, and Nick, and many others have helped me become a better teacher and mentor – skills that I know will be important to me in the future – as well as accomplishing mountains of research.

Finally, the Velegol lab is what it has been for me solely on the efforts, dreams, and vision of one person: my advisor Professor Darrell Velegol. Darrell is an excellent scientist – I’ve rarely seen anyone’s face light up so much in the middle of an ‘exciting’ derivation. He is also a great writer and thinker, always knowing how to ask the right questions to frame the work we’ve done. However, where Darrell excels the most is in his abilities as a mentor. I have honestly never met anyone so dedicated to serving the individual needs of the people in his charge. He is capable of being entirely different from person to person and from day to day, tirelessly working to serve the needs of each individual at each moment. Through his help and support, I have decided to pursue a career in academic, in no small part due to the inspiring figure
of a leader I have worked with these past five years. For that, and for so many other things, I owe Darrell my deepest gratitude and respect.

My time in grad school has not always been easy (for reasons that have nothing to do with work), but the Chemical Engineering department here at Penn State, all of its staff and faculty, and especially my fellow graduate students, have been there for me in ways too numerous to count. I also must thank my thesis committee, Profs. Michael Janik, Themis Matsoukas, and Ayusman Sen, for all their time and effort throughout the years, and especially these last few weeks given the rushed nature of this thesis and defense. In particular, Prof. Sen has been an outstanding collaborator to our group, involving us in so many new projects and ideas, and always willing to listen to the ‘Chemical Engineering’ perspective. His guidance, especially in the past year, has been truly invaluable, and he has always pushed us to shoot higher and be better in everything we do.

Outside of the crazy world of graduate school, in fact, outside of this crazy town of State College, lies the city of Rochester, NY. There in that city, for the past five years, has been the love of my life, my beautiful fiancée, Ashley Anderson. Our relationship hasn’t always been easy, with 3.5 hours of distance, but it has been essential. Everything we have done, together or apart, since college, has continued to bring us closer to our goal: finally being together (in the same place!) - now hopefully less than a year away. Ash brings out the best in me, keeps me in check, handles my stress, and lets me return the favor. I can’t wait to start my life with her.

Finally, at the end of all these acknowledgements, I find myself back at the beginning: thanking my family, especially my parents. I thank my mother, Michele Mc Dermott, for her guidance and support, but more importantly for her compassion and kindness. She has set an example for me to live by every day, and will always have a place in my heart (and in the back of mind), helping me to do what is good and what is right. And lastly, I am a very lucky person: a
love of Penn State wasn’t the only legacy my father, Joseph M. McDermott, gave to me. I don’t really have the words for how big of an impact my father has had on me, so this will have to suffice: I will spend a lifetime following in his footsteps, and if I end up just a fraction of the person he was, I will consider myself truly blessed.
“The really important kind of freedom involves attention, and awareness, and discipline, and effort, and being able truly to care about other people and to sacrifice for them, over and over, in myriad petty little unsexy ways, every day. That is real freedom. The alternative is unconsciousness.”

-David Foster Wallace

“Destiny is what we work toward. The future doesn’t exist yet. Fate is for losers”

-Douglas Coupland
Chapter 1

Motivation and Research Goals

1.1 Motivation and Background for the Work

1.1.1 Colloids and Commercialization

Colloidal assembly is undergoing a renaissance of sorts. What began as a means to an end for individual applications has become an independent field with equal contributions from physicists, chemists, chemical engineers and materials scientists. Both the colloidal systems being studied and the assembly techniques being developed are increasingly diverse and complex. With progressively more control over particle functionalization, the development of template- and field-driven assembly techniques, and novel manipulation of solution conditions, model assemblies of colloidal particles can be found in all shapes, sizes, and material types.

As-synthesized colloidal particles have found many uses in industry, from historic applications in inks, paints, and food additives,\(^1\) to more recent applications in displays\(^4\), microfluidics\(^5\), photonics\(^6\), chemical-\(^7\) and bio-sensing\(^8\) and capsule fabrication for delivery and transport\(^9\). While synthesis of multimetallic colloidal particles can be difficult, synthesis of single metal particles is much easier. Gold nanoparticle sols were synthesized by Faraday in the 1800s\(^2\). Expanding on the basic chemistry of this synthesis, many types of metallic dispersions with individual particle sizes from nanometers to microns have been formed in recent years. In fact, recipes for colloidal dispersions of various sizes and materials are readily available in field-specific journals such as *Langmuir* and *Journal of Colloid and Interface Science* as well as more general publications such as *Journal of the American Chemical Society* and *Physical Review*.
Letters. In many cases, these syntheses can be scaled to create large volumes of particles within tight specifications. As a result, commercialization of specialty colloid products has begun, with companies such as Interfacial Dynamics Corporations selling polystyrene latex particles with buyer-dictated sizes and functionalities.\textsuperscript{10}

Commercialization of assembled or fabricated colloidal particles (i.e., particles made of two or more preexisting component particles assembled into a single structure and held together by interparticle forces), however, is considerably more rare. To promote commercialization, one of the primary challenges on the horizon for all scientists studying colloidal assembly is the development of useful and functional assemblies. In other words, while we have the bin full of individual Legos and we understand how they fit together, we don’t know if we’re building a house, a spaceship, or just a random pile of bricks. This problem is compounded by the fact that many assembly techniques work only with very specific colloidal systems. For example, complex assemblies of particles in alternating electric or magnetic fields may exhibit their unique behavior only for particles of a certain size and material type.\textsuperscript{11,12} Other physical assembly techniques, such as microfluidic cojetting\textsuperscript{13} or monomer swelling and dewetting\textsuperscript{14}, rely on specific particle-solution interactions to induce phase separation. In addition to the restrictive specificity of these assembly techniques, there is also the problem of scale. Techniques such as assembly in microfabricated templates\textsuperscript{15,16} often cannot produce a useful number of particles to have any realistic industrial applications.

Fabrication techniques that are both scalable and general enough to show promise for producing large numbers of functional colloidal assemblies are control of aggregation\textsuperscript{17,18}, assembly in microfluidic networks,\textsuperscript{19} and assembly at interfaces\textsuperscript{20}. The expertise of the Velegol lab group is in the manipulation and control of colloidal aggregation, by controlling dispersion thermodynamics\textsuperscript{18} and through site-specific functionalization of individual particles.\textsuperscript{21} Our assembly techniques are designed to be specific enough to build functional assemblies with
desired structures or particle orders, but generalized enough to be used for a large number of systems. Additionally, we strive to take the scalability of our techniques into account, although this work does not demonstrate any experimental attempts made at scale-up.

1.1.2 Colloidal Motors are Ideal as Complex, Functional Assemblies

The chemistry behind the colloidal motor systems built in this work was initially developed by Professors Ayusman Sen and Tom Mallouk in the Department of Chemistry at Penn State University. Transition metals have long been known to catalyze the decomposition of hydrogen peroxide. When two transition metals with different work functions and thus different catalytic activities are placed into electrical contact in a peroxide solution, the two half reactions of the catalyzed decomposition reaction will take place preferentially on the two different metals. The metal functioning as the anode oxidizes a peroxide molecule into protons, electrons, and oxygen gas. The proton and electron reaction products then travel to the metal functioning as the cathode, where they reduce another peroxide molecule to form water. Figure 1.1 shows a schematic of this system. While the oxidation and reduction reactions are necessary parts of the motor’s chemistry, it is the transport step of protons and electrons moving from the anode to the cathode that drives the autoelectrophoresis of the assembly. The electron moves easily through the assembly, travelling in conduction bands from one metal to the other, overcoming a slight diode potential in the process (trivial as the overall cell potential for the decomposition reaction is 1.094 V vs. SHE). The proton, however, must move through solution to reach the anode. Of course, protons are readily available in water, so it is easier to think of the solution surrounding the anode as proton-rich and the area surrounding the cathode as a proton-depleted. The ionic gradient of protons in the solution surrounding the motor acts as a localized
electric field. Any surface charge on the motor will cause it to move in response to the applied electric field.

![Figure 1.1: Schematic of a bimetallic colloidal motor. Peroxide oxidation occurs on the gold surface. The electrons and protons generated travel through the metals and surrounding solution, respectively, where peroxide reduction take place on the silver surface. This flow of protons results in a localized electric field that drives the motor’s motion based on its surface charge.](image)

It should now be clear why this assembly can be considered a motor: it consumes fuel (peroxide) to propel itself through a solution in the direction of the electrochemical reaction. The first colloidal system to demonstrate this behavior was a gold-platinum nanorod. Gold and platinum are both attractive metals to use, as they are inert in a wide range of potentials and pH and are both strongly catalytically active. These nanorods (on the order of 300 nm in diameter and 2μm in length) were synthesized by electroplating the metals onto a silvered alumina template. The template was then dissolved and the rods suspended in solution. The primary advantage to this technique is that the gold and platinum metals are (necessarily) in electrical contact due to the electroplating, and electron transport from the anode metal to the cathode metal is necessary for motor activity. Unfortunately, production of large quantities of the nanorods thorough this method is costly and time consuming. While the overall control of the synthesis is strong, varying the rod materials is nontrivial.
Colloidal motors are excellent examples of complex, functional assemblies. They are typically multicomponent particles or assemblies made of specific materials arranged in a specific way. They perform a task (autonomous movement) in response to a stimulus (here, hydrogen peroxide), and therefore have a definite function. In this work, I work to expand on existing motor technology in two ways: First, by integration of a third material (which I will term the ‘gate’ material) between the anode and cathode metals of the motor, I will attempt to regulate the flow of electrons in the motor and therefore control the motor’s activity. The obvious choice for a generalized gate material is an undoped semiconductor. By choosing a material, cadmium sulfide, that has inherently low conductivity (i.e., fully insulating) at ambient conditions I can assure the motors are not initially active. Because CdS has a bandgap in the shortwave visible light region, I can increase the conductivity of the gate material by exposing it to blue/green light, activating the motor. Ideally by varying the intensity of the light, I can externally control the speed of the motor.

By assembling this improved motor setup rather than synthesizing it outright, the opportunity arises to craft a generalized assembly technique that allows for rapid prototyping of various gate, anode and cathode materials. This is the second improvement on the existing motor design. This assembly is more complex than many previous assemblies my lab has fabricated, but it also represents the next logical step in assembly work in the Velegol lab. We have made homodoublets\textsuperscript{18}, heterodoublets\textsuperscript{18,21}, site-specific functionalized particles and capsules\textsuperscript{21,28}, and even a colloidal ‘water’ molecule made of two different materials\textsuperscript{29}. The motor is essentially a ‘trimer’ of three different materials. These materials must be assembled in a specific fashion (anode touching gate touching cathode), and the assembly technique must be as general as possible. The accomplishment of this task gives us a quick, inexpensive way to assemble motors of many different materials that can be tested against the idealized gold-platinum nanorods on which the work was founded.
1.2 Research Goals

In this dissertation, I look at the process of colloidal assembly, specifically in the context of catalytic motor particles, from start to finish, and set forth the following research goals:

1) Assemble a ‘traditional’ bimetallic catalytic motor from component metal microparticles, and assess its motility in hydrogen peroxide.

2) Work to analyze the movement of assembled motors and surrounding particles owing to localized, self-generated electroosmotic and diffusioosmotic flowfields.

3) Craft a generalized, flexible assembly technique that allows for the fabrication of three-component, ordered ‘trimer’ particles.

4) With the knowledge gained from goals (1) and (2), and the assembly technique developed in goal (3), design and fabricate a three-component, photoactive catalytic motor.

5) Explore separation techniques capable of separating colloidal particles by size, shape, or other distinguishing factors that take advantage of the singular complexities of concentrated distributions of colloids.

These goals encompass a large number of scientific disciplines and make use of a wide variety of experimental and analytical techniques. In exploring the science behind colloidal assembly, I have come to appreciate the complexity and beauty behind this truly interdisciplinary field.
1.3 Dissertation Outline

1.3.1 General Overview

This dissertation documents the research involved in the assembly and purification of complex, functional colloidal devices. Chapters 2 through 7 are taken directly from, or are expanded versions of published, submitted, or in preparation technical research manuscripts. Additionally, Chapter 2 gives an analysis of colloidal assembly as a chemical engineering process, and discusses how this analysis relates to the work in this dissertation. Assembly techniques found in Chapters 4 and 5 are used throughout the dissertation. Each chapter contains an introductory section that reviews the relevant literature and discusses the main ideas of that chapter, and the experimental chapters (3 through 7) contain experimental sections discussing techniques and materials used. Chapter 8 contains conclusions and possible future work. Relevant permissions are given at the end of each chapter, along with a list of references.

1.3.2 Chapter 2: Colloidal Assembly as a Chemical Engineering Process

In this chapter, clear parallels are drawn between bulk chemical production processes and colloidal assembly, which is termed as taking place in ‘micro-factories.’ Just as a chemical synthesis process has clear inputs and outputs around traditional unit operations, colloidal assembly has the metaphorical flow of particles in and out of assembly, surface modification, separation and sonication processes, even including options such as recycle and waste streams. A simple diffusion-limited aggregation process is described in detail. A process flow diagram for this process is shown, various unit operations are discussed. The chapter concludes by applying the analogy to the various assembly and separation processes specifically used in this dissertation.
1.3.3 Chapter 3: Effective Density Sorting of Soft Colloidal Spheres

In this chapter, we examine the phenomenon of ‘effective density sorting’ where a close-packed but mobile sediment of heterogeneous colloidal particles spontaneously separates into layers with constant particle volume fractions. This behavior can be explained and modeled by analyzing and minimizing the gravitational potential energy of the system, taking into account both the effective density of each mobile colloidal particle + double layer, and the effective density of each layer due to the change in random packing fraction as a function of particle composition. This sorting phenomenon is unique because it occurs specifically because of gravity – not in spite of it – and works best for high concentrations or solids loadings of particles (up to and beyond the random close packing limit of 0.64) and may eventually lead to both high-throughput colloidal separation techniques and new ways to measure bulk interparticle forces.

1.3.4 Chapter 4: Simple Fabrication of Gold-Silver Heterodoublet Motors

In this chapter, the stimulate-quench-fuse (SQF) method of colloidal assembly is used to fabricate heterodoublets of micron-sized gold and silver particles. The aggregation statistics and stability of the motors are analyzed. Due to the high Hamaker constants of the materials, the metal doublets withstand long-term sonication much better than polymer or oxide aggregates. The particle motility is also studied, by observing the movement of heterodoublet motors in hydrogen peroxide. It is shown that there is enough electrical contact across the gold-silver interface between the two aggregated particles to allow the motor to function normally. In one case, a motor is observed breaking apart in solution, after which all motion ceases.
1.3.5 Chapter 5: Colloidal Trimers Fabricated Through Quenched Electrostatic Assembly

Three-component assemblies are constructed, having a specific order (particle 1 – particle 2 – particle 3) but no specific orientation (‘bond angle’). The technique used to do this is developed in this chapter – Quenched Electrostatic Assembly. In QEA, the central ‘core’ particle is functionalized to have one sign of charge, while the other two ‘satellite’ particles have the opposite sign of charge. Aggregation is done in low ionic strength, so all electrostatic forces are present. These experimental conditions prevent satellite-satellite aggregation, although considerations must be made for core and satellite number densities to prevent bridging two cores with a single satellite, leading to higher ordered aggregation. The aggregation is ‘quenched’ but addition of a charged nanoparticle or polyelectrolyte with the same sign as the satellites. This quickly coats the core and restores stability to the system. The QEA technique is tested on six different trimer systems (both 2- and 3-component). Statistics are performed to understand how to optimize the QEA technique for any given satellite/core/satellite configuration.

It is shown that fusing the nanoparticle / polyelectrolyte quench coatings leads to a large increase in mechanical stability in the trimer – the fused trimers hold up significantly better under sonication than those that have not been fused. One ‘active’ three-component trimer is fabricated: a gold-silicon-silver trimer that functions as a catalytic motor in hydrogen peroxide. Unfortunately, this trimer lacks the ability to be controlled by light due to the overly high native conductivity of the silicon core.

1.3.6 Chapter 6: Dissolution-Induced Fluid Pumping in Disturbed Geologic Formations

In addition to peroxide decomposition-based electrophoresis, auto-diffusiophoretic motors have been studied. In order to fully understand the mechanisms inherent to the complex
three-component motors fabricated in Chapter 7, we must first understand how ionic gradient
diffusiophoresis and osmosis can effect flows in charged colloidal systems. Calcium carbonate,
a material ubiquitous in nature and commonly used in biocolloidal systems, is shown to generate
localized ion gradients around its surface when suspended in CaCO$_3$-unsaturated water, due to
partial dissolution of the material. Calcium carbonate microparticles are synthesized. Although
not mobile themselves, the particles slowly dissolve into solution and, owing to the difference in
diffusion coefficients of the resulting ions, set up powerful electric fields surrounding them that
drive flow both of individual tracer particles and at bulk charged interfaces, such as glass
substrates. In this chapter, the diffusiophoretic ‘pumps’ are compared with diffusiophoretic
heterdoublet motors of polystyrene latex colloids and CaCO$_3$ microparticles fabricated using the
QEA technique, as well as flows generated by large natural rock samples of dolomite, calcite,
barium carbonate, and gypsum. By better understanding the mechanistic differences between
autodiffusiophoresis (Chapter 6) and autoelectrophoresis (Chapter 4), we can run more informed
experiments with the three-component motors from Chapters 5 and 7.

1.3.7 Chapter 7: Photoresponsive Metal - Cadmium Sulfide Colloidal Micromotor Assemblies

In this chapter, three-component, photoresponsive noble metal-semiconductor motors are
fabricated using the QEA technique. The use of cadmium sulfide as a ‘core’ semiconductor gate
material between a gold and a silver satellite is shown to be highly effective at controlling motor
activity as a function of incident light. In the absence of any strong blue light, the particles are
motionless, even in 0.1% hydrogen peroxide solution. At lower light intensities, the motors
become active, moving in a very similar manner to gold-silver heterodoublets. Comparison are
made by observing both the motion of the motor and the motion of polystyrene tracer particles
within the localized flowfield of the motor. At higher light intensities, however, a strange
phenomenon occurs: the motors tend to adhere themselves to the glass substrate, and start diffusiophoretically pumping particles, similar to the calcium carbonate pumps in Chapter 6. Even more unusual is that this behavior does not seem to be limited to peroxide solutions – it occurs in DI water as well. By combining our understanding of autoelectro- and autodiffusiophoresis from previous chapters, we comment on possible explanations for this observation.

1.3.8 Chapter 8: Conclusions and Future Work

This chapter summarizes the dissertation with respect to the research goals and discusses possible future work in three distinct areas: separations, ‘intelligent’ motor development, and engineering diffusiophoretic flows in mineral systems for enhanced particle and transport in pores.

1.4 References


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Chapter 2

Colloidal Assembly as a Chemical Engineering Process

2.1 Introduction

Niche markets are often well-served by small producers able to adapt quickly to localized demand. America’s brewing industry provides one example through its recent history.\(^1\) Currently about 90% of the domestic market share for beer – roughly 200 million barrels or 6 billion gallons – is in the hands of Anheuser-Busch, Miller, and Coors. And yet, the number of specialty brewers grew from 10 in 1980 to more than 1300 by the year 2000.\(^1\) Microbrewers and brewpubs produce less than 15,000 barrels per year, but they focus on high-quality products adapted to particular customers. By having prices 50% higher than usual pale lagers, requiring far less advertising, and even taking advantage of local tax laws, a specialty brewer can produce a gross revenue of a few million dollars per year.

This chapter explores the development of processes for another category of niche markets: colloidal assemblies. Although colloidal particles have been used for millennia, the concept of assembling nano-scale or micro-scale particles into small “colloidal devices” or “colloidal machines” is a rather recent development.\(^2\) Simple devices, such as colloidal motors\(^3^,^4\) or colloidal barcodes\(^5\), have already been fabricated and studied, at least at the research level. Rather than producing 1 million metric tons per year of commodity vinylacetate or styrene butadiene particles, like BASF or Dow, we explore how companies can develop processes that fabricate specialty colloidal assemblies, perhaps in batches of 10 to 100 grams with a rapid turnaround time, by designing colloidal micro-factories. Initially such specialty producers of colloidal assemblies might primarily serve research needs for other small or large companies;
however, with time, commercial markets might emerge for a greater number of specialized products. The over-arching question in this chapter is this: Can small, nimble, smart businesses carve out niches in producing specialized colloidal assemblies? In examining this question, we explore four main points:

1) Colloidal assemblies are high-value specialty products.
2) Control of interparticle forces enables “bottom-up” processes for making assemblies.
3) Micro-factory processes are adaptable, small, and have low capital investment.
4) Chemical Engineers are well-positioned to design and operate colloidal microfactories.

As entrepreneurs become willing to engage in these small ventures, the micro-factory approach for producing assemblies can add significant value, especially for initial research and development operations, and later in aiding the commercialization of technologies that result from the R&D.

2.2 Background

2.2.1 Colloidal Assemblies are High-Value Products

Synthetic rubber demand during World War II caused an enormous scaleup of polymer colloid production. Worldwide there are now more than 500 companies that produce and sell polymer colloids. The three leading suppliers, BASF, Dow, and Rohm and Haas, each has the capacity to produce more than 1 million metric tons (wet) per year, accounting for 20% of polymer colloids produced annually. The particles are typically sold as commodities: a gallon of paint costs roughly $20, while a bottle of wood glue might cost $5. Common polymer colloids,
such as styrene-butadiene copolymers, polyacrylates and vinyl acetate homopolymers and copolymers, are used in applications from leather finishing to printing inks.\textsuperscript{6,7}

In contrast to these bulk markets, small companies such as Polysciences, Invitrogen (through Interfacial Dynamics), Bangs Laboratories, Duke Scientific, and other manufacturers produce particles primarily for research purposes.\textsuperscript{8} These particles have tight specifications (e.g., size distribution) and good quality control, and they are high-value; our lab typically purchases a dozen 15 mL bottles of 8\% solid monodisperse polystyrene nano and microparticles per year, each of them costing more than $150. By mass, the cost for the polymer particles is 3 to 4 times that of gold. Particles with specialized functionalities such as ligands or fluorescent groups cost even more, and the demand for small amounts of the customized particles remains significant.

Colloidal assemblies that function as “colloidal devices” will in general be even more complex than their constituent particles. As a result, they will have even higher value added. In 1998 Jacobson and co-workers published their work concerning a capsule, in which tiny dark or light particles could be moved electrically.\textsuperscript{9} This research has now turned into E Ink, the Cambridge, Massachusetts-based company that produces the display technology for the Amazon Kindle and the Barnes & Noble Nook. There are many more types of smart particles on the way, including the mobile microscale and nanoscale motors mentioned earlier\textsuperscript{3,4} which are environmentally responsive, and can perform chemotaxis in the manner of motile bacteria.\textsuperscript{10,11}

\textbf{2.2.2 Control of Interparticle Forces Enables “Bottom-Up” Processes}

In recent years the concept of colloidal molecules\textsuperscript{12} has emerged, in which colloidal particles are treated analogously to atoms and molecules in molecular chemistry. Glotzer and Solomon established a “periodic table” concept\textsuperscript{13}, in which the constituents are not atoms, but nanoscale or microscale particles with various morphologies, size, material composition, and
other defining characteristics. Many unique assemblies have already been fabricated, including
doublets, \(^{14,15,16}\) “colloidal water”, \(^{14,17}\) and grape-like clusters. \(^{18}\) Most of these have been produced
using bottom-up assembly, at least in some steps, which usually corresponds to less expensive
processes. In bottom-up assembly, a chemistry is patterned onto the particle surfaces so that the
particles are “chemically programmed” thermodynamically to favor specific assembly. The
potential combinations for assembly are immense in number, and many of these particles have in
fact been comprehensively reviewed.\(^{19}\)

Two key barriers remain in using bottom-up techniques to fabricate colloidal assemblies.
First, most techniques allow only a limited number of particle materials to be used, for instance
certain polymer types or certain metal types. The challenge here is that sophisticated colloidal
assemblies or devices might often require \emph{combinations} of various polymers, oxides, metals,
semiconductors, or hydrogels. Additionally, specific applications sometimes require that various
materials be compared for performance in a given application. In contrast to molecular
chemistry, in which covalent bonds dominate, colloidal assembly is usually governed by physical
interactions\(^{20,21}\) and these forces are readily manipulated. Van der Waals forces, hydrophobic
forces, electrostatic forces, and similar physical phenomena – many of which are readily
controlled by changing the solution or ambient conditions, provide an enormous toolset by which
to assemble a broad range of particles.

Although there are differences between molecular synthesis and colloidal fabrication,
numerous analogies may also be made. For example, template-based assembly may be
considered a type of heterogeneous catalysis which combines some aspects of bottom-up and top-
down assembly. Controlled assembly, occurring either when “patchy particles” bond at specific
sites or when bare particles bond during a certain time period, may be considered a type of
homogeneous reaction.
The second key challenge is that most assembly techniques produce only small quantities of particles, say milligrams at present. While this is sufficient to publish a high-impact image in a journal, it is considerably less than the 10 to 100 grams or more required even at a niche commercial level. As assemblies used for research lead entrepreneurs to assemblies with potential application in broader commercial uses, even larger quantities will need to be produced. This requires that we consider colloidal assembly in a manner beyond traditional methods. We will need to start considering entire processes for producing the assemblies.

2.2.3 Microfactories Have Quickly-Adaptable, Batch Unit Operations

Continuous processes have little merit for the small-scale fabrication of assemblies. The primary costs will be in rapid engineering and prototyping, rather than in equipment capital investment or sometimes even raw materials. Small batch or semi-batch unit operations will likely prevail, many of which are already used in laboratories around the world. As a result, capital expenses for the equipment will be low and the operations will require minimal commissioning time. Moreover, the small batch process enables users to morph a process quickly, in order to produce custom particles and assemblies. Thus, sophisticated process control schemes can often be avoided, and if product quality is insufficient, the next batch can be optimized and processed.

As an example of a micro-factory design, consider the “stimulus-quenching-fusion” method for producing doublets. This process is used to form the heterodoublet motors in Chapter 4. A process flow diagram (PFD) of the process is shown in Figure 2.1. Spherical particles with diameters \((2a)\) from several micrometers down to less than 100 nm are fed into a batch reactor. The particles might be negatively-charged in aqueous solution, with a surface potential \((\psi_0)\). Ordinarily, we seek colloidal suspensions in which the particles do not aggregate.
(i.e., they are “stable”), with a large magnitude of $\psi_0$ (corresponding to highly negatively charged particles due to dissociating carboxyl, sulfate or other groups on the particle surface). Such particles have significant repulsive electrostatic forces, which maintain a gap ($\delta$) between the particles. The electrostatic forces work against the attractive van der Waals forces, which are stronger for material systems with a higher Hamaker constant ($A$). A simplified version of the interaction potential between two particles, commonly known as the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential energy, is

$$\Phi = 2\epsilon a \psi_0^2 \exp\left(-\kappa \delta\right) - \frac{aA}{12\delta}$$

Eq. 2.1

where $\epsilon$ is the permittivity for water and $\kappa^{-1}$ is the Debye screening length. The Debye length, which is readily calculated from the solution conditions,\textsuperscript{21} serves as the characteristic length scale over which particles interact electrostatically in an ionic solution. A plot of Equation 2.1 for $\Phi(\delta)$ reveals a potential energy barrier between particles, analogous to an activation energy barrier in transition state theory.

Using Equation 1 as a guide, we can manipulate the potential energy between particles. By increasing the ionic strength, we can decrease the Debye length and lower the potential barrier, allowing particles to aggregate together.\textsuperscript{20} We could solve for the case when the potential energy barrier indicated by Eq 2.1 (or more complicated and accurate expressions\textsuperscript{20,22} for the energy) is small enough to allow aggregation, but in practice, we know that having 1.0 M KCl solution gives a Debye length of 0.3 nm, which is small enough to allow rapid, diffusion-limited aggregation of the particles. The particles do not, however, simply clump up instantaneously. Their aggregation is diffusion-limited, like many reactions. Singlets form doublets; doublets
combine with singlets to form triplets; doublets combine with doublets to form 4-lets, and higher order aggregates continue to form.

If we have a volume fraction ($\phi$) of particles, we could solve the population balances to determine the entire range of aggregates as a function of time. On the other hand, we can treat the aggregation of singlets as a binary reaction given by the usual rate expression 

$$r_i = \frac{dn_i}{dt} = -kn_i^2,$$

and then use several equations from colloid science to find that the rate constant is given by 

$$k = \frac{8k_BT}{3\eta},$$

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $\eta$ is the viscosity of the suspending solution. Using these equations, we can estimate a time constant ($\tau$) for diffusion-limited aggregation as

$$\tau = \frac{\pi\eta r^3}{k_BT\phi}$$

Eq 2.2

By decreasing the ionic strength or other stimulus, we can increase this time scale to many times this diffusion-limited result, usually in a controllable manner. Thus, a few simple estimates from colloid science have given us an equation to relate parameters easily controlled in solution, and this equation is often sufficient as a starting point to predict and reliably scale up the aggregation step.

In continuing the process, we “quench the reaction” after the rapid aggregation time by diluting with water to decrease the ionic strength. This increases the repulsion between the particles. In some ways the high ionic strength has served as a catalyst for the reaction. If one of the particle types is polymeric, we can make the doublets very mechanically stable by raising the temperature above the glass transition temperature of the polymer, allowing the particles to fuse. Finally, since the random aggregation step has given un-aggregated singlets, the desired doublets, and some side products (triplets and higher order aggregates), we require a sorting or separation
Techniques such as hydrodynamic chromatography and field flow fractionation can sort singlets (which are recycled to aggregate again) from doublets (which are stored for use) from side products (treated as waste). Currently these sorting operations are done at a very small scale.

We have discussed the design of a micro-factory for producing a simple type of colloidal assembly (i.e. doublets), using a process flow diagram. Similar process flow diagrams can in principle be designed for the formation of more complex types of assemblies, thereby creating micro-factories for the fabrication processes.

Colloidal micro-factories can fit in a single room, and perhaps even on a tabletop, since the “unit operations” are small. Furthermore, the equipment can be assembled quickly, with sufficient design knowledge. For companies wanting rapid prototyping of an idea, these factories will serve an important purpose, as a process can transition from conception of the idea to reception of the assemblies within two months, by contracting a niche company. Currently, many particle assemblies are produced using the beakers and flasks on a laboratory bench, or a small microfluidic network created at a nanofabrication facility. To a Chemical Engineer, however, that same beaker resting on a bench top serves as a “batch reactor”; a centrifuge or rack of test tubes for settling is an effective separator; a microfluidic network or syringe pump acts as the transport system, while an autoclave or water bath functions as a heat exchanger. Both the materials and methods scale down for micro-factories, although in addition to the usual design parameters like viscosity, heat capacity, and diffusivity, colloidal processes involve parameters such as zeta potentials (surface potentials on particles in solution), ionic strengths and double layer thicknesses, surface tension, surface adsorption, and Hamaker constants.21

When optimizing yields of the colloidal assemblies, one of the most critical yet daunting unit operations is sorting or separations. There is no equivalent of a distillation column for micron-size particles. Although small-scale, analytical sorting techniques such as field flow fractionation and hydrodynamic chromatography exist, the ability to sort 1 to 100 kg per year of
material is a significant challenge – one that the authors of this article have been studying for more than 5 years.\textsuperscript{23,24} Processes such as field flow fractionation, hydrodynamic chromatography, or density gradient centrifugation can be used to sort assemblies, but they are limited in throughput. Sorting is an important research need for colloidal assemblies.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{batch_process_diagram.png}
\caption{Process flow diagram for batch process to assemble doublets. Just as molecules are fed as inputs into a process, here colloidal particles are fed into a batch reactor. After the designed colloidal aggregation occurs, we have “unreacted” single particles, doublets (the desired product), and a small quantity of triplets and other undesired higher order aggregates (side products). The assemblies go through an autoclave to fuse at 118 C, and then they go through a separator (e.g., a field flow fractionator,), after which singlets are returned to the reactor, doublets are stored, and other products are treated as waste.}
\end{figure}

Due to the size of the equipment and its availability, a great advantage of colloidal microfactories is the need for lower capital investment relative to larger factories. Designing processes
at the nanoscale or microscale opens up possibilities for integrating unit operations in new ways, for instance using some surface techniques for both assembly and sorting. Moreover, the small size of the micro-factories translates to a greater potential for safer processes, as many assembly techniques are performed in aqueous solution at ambient temperature and pressure. Still, it is imperative that a thorough safety analysis be performed, and HAZOPs and operability guidelines be generated regardless of the size of the micro-factory. Although waste product volume is minimal, that material must be handled responsibly.

2.2.4 Conclusions and Outlook

An irony of colloidal micro-factories is that while the materials being synthesized – colloidal particles instead of molecules – are individually larger than molecules, the factories used to produce them will be much smaller than for most molecular processes. Some of the organizations mentioned earlier that produce specialty particles might well be interested in incorporating new sections into their factories … in rooms in already existing facility. That is, already-small factory buildings can house even smaller colloidal micro-factories.

Micro-factories need not address only niche commercial markets. Multifunctional colloidal assemblies can be designed for water remediation, drug delivery and other meaningful applications as a result of the tremendous design flexibility characteristic of micro-factories. An additional benefit of the smaller footspace is portability, such that microfactories can be inexpensively built or delivered to various parts the world. Delivery speed, both locally and internationally, is important, and requires a reduction in specialization so that one person (or a small team) can effectively identify the need, rapidly develop relationships, design and build the micro-factory, and sell quality products that generate profit.
Several critical barriers have been addressed in this section, concerning the advancement of colloidal micro-factories. Technical issues in colloidal fabrication and sorting are currently being addressed in research labs around the world. Important engineering challenges exist in rapid design and scaleup of not just fabrication techniques, but entire processes for producing assemblies. Building teams who understand outside technical issues, including molecular biology, medical applications, or polymeric applications, is crucial. Addressing local, niche markets requires a detailed knowledge of local contexts as well as specialized science and technology and implementation with integrity.

2.3 Microfactories in the Context of this Dissertation

As a colloid scientist, I have often found myself thinking on a very small scale – much smaller than the towering diffusion columns and voluminous CSTRs of my college courses. However, by treating the colloidal assembly process as a Chemical Engineering process, analogues, I have always been able to frame my work in the context of that process. This has proven especially useful when communicating my ideas to scientists and engineers without formal colloidal science training. While it might be difficult explaining the SQF process as a research idea, it becomes much easier when you can frame it as a ‘micro-factory’ process, as discussed above.

This dissertation, and, indeed, much of the work in the Velegol lab, focuses on two specific steps of the PFD found in Figure 2.1: the batch reactor / quench tank, and the separator. The reactor and quench tank, as mentioned earlier, is analogous to any colloidal assembly process. I have developed and implement two assembly processes in this work: the SQF aggregation process described here and used in Chapter 4; and a more complex diffusion-limited process called ‘quenched electrostatic assembly’ (QEA), which is developed in Chapter 5, and
used in Chapters 6 and 7. These assembly processes are not complex in principle – they require very little specifics – but they are also uncontrolled, akin to chemical reactions that do not always go to completion and that produce unwanted by-products. In the case of diffusion-limited assembly, the ‘product’ particles tend to be more of a distribution than a single entity, owing to the statistical nature of aggregation kinetics.

The complexity of any given diffusion-limited assembly process can typically be increased through the addition of surface functionalizations and anisotropy to the ‘reactant’ particles, leading to localized interparticle forces and a more directed approach to the assembly. In some sense, the QEA technique is a ‘next-level’ process that arises from SQF, i.e., through the addition of specific electrostatic forces, we can build ordered assemblies and prevent unwanted particle aggregation. The cost of added complexities is not just a material cost. More complex particles may lose some component of their functionality (e.g., particles with catalytic surfaces may be hindered by surface modification), and the more complex processes often take longer and are harder to scale-up. Therefore, a strong motivation for all the work in this dissertation is balancing assembly complexity with practicality, working to retain flexibility and scalability throughout.

The second part of the Fig. 2.1 PFD this dissertation addresses is the separator. As mentioned above, colloidal particles are much more difficult to separate than molecular compounds, due to both the inherent physics (colloids are much more likely to be affected by gravity, have much smaller diffusion coefficients, and can act as complex fluids at moderate volume fractions), and due to a lack of current technologies for high-throughput sorting of distributions of colloidal particles and assemblies.

Chapter 3 discusses a colloidal separation technique that I have developed with my labmate Cesar Gonzalez Serrano called effective density sorting. The primary appeal in this technique is that it can be used in concentrated suspensions of colloidal particles. In fact, the
underlying phenomenon is only observable at high solids loadings and in the presence of gravitational forces. In addition to the relevant underlying science behind effective density sorting, the technique offers a key component to this dissertation: the possibility of high-throughput sorting of assembled colloids from their component particles and other unwanted structures.

2.4 Acknowledgements and Copyright Information

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Although this work was originated by Darrell, many of the central ideas and framing came from prolonged discussion between all the authors and the writing and figure preparation was split between us. I thank Darrell for including me in this work and all my fellow authors for their contributions and enlightening discussions.
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Chapter 3

Effective Density Sorting of Soft Colloidal Spheres

3.1 Introduction & Background

Colloidal suspensions often contain mixtures of particles that must be sorted by size or density. One route to sorting gram-size quantities of particles is sedimentation, which has been studied for decades from both dynamic and thermodynamic perspectives. Dynamic predictions for settling account for hydrodynamic\(^1\), colloidal\(^2\), and electrophoretic\(^3,4\) interactions at finite volume fractions (\(\phi\)), but in the final sediments the particles are usually non-mobile. Thermodynamic studies have examined colloidal crystals,\(^5,6,7\) but primarily for the case of mono-disperse particles settling at low Peclet number.\(^8,9,10,11\) An important question remains unanswered: What sediment structure results when bi-disperse or poly-disperse particles settle rapidly, forming amorphous and mobile sediments? Here we show that bi-disperse colloids having soft-sphere interactions spontaneously arrange into two macroscopic layers after a sedimentation process, even at Peclet number greater than order unity. The layering can be explained without appealing to complex hydrodynamic or thermodynamic arguments; rather, the layering is readily explained simply by minimizing the free energy of the system, which is primarily the gravitational energy for our cases. Furthermore, minimizing the energy of the system leads one to expect an “asederotrope”, an azeotrope-like mixture of particles in one or both of the layers that is seen in our experiments. Our results may lead to designs for preventing de-mixing of colloidal products during shipment, for improving sorting or size-refinement operations for colloidal particles of different size or density, for sorting mixtures of biological components, or for purifying mixtures of colloidal assemblies.
3.2 Experimental Methods and Materials

3.2.1 Sedimentation Sample Preparation and Materials

1 ml of particle suspensions at 0.01 volume fraction was prepared for the following particles: 0.99 µm white Sulfate (CV: 2.5%, Batch No. 8890) PSL 2.0 µm green Sulfate PSL (CV: 2.6%, Batch No. 1-GN-2K. 1, DI water is $\zeta = -43.81 \pm 3.11$ mV) and 3.0 µm red Sulfate PSL (Coefficient of variation: 3.5%, Batch No. 1-GN-2K. 1, $\zeta$-potential in DI water is $-57 \pm 4.2$ mV) bought from Interfacial Dynamics Corporation (Portland, OR); 3.0 µm Silica (Batch No. 5411, $\zeta$-potential in DI water is $-62 \pm 6.6$ mV) bought from Bangs Laboratories, Inc (Fishers, IN) and 150 nm gold particles produced from the reduction in solutions of gold ions with gum arabic over 1 hour as described by Handley. The measurements of $\zeta$-potential were taken using a Zeta Potential Utilizing Phase Analysis Light Scattering instrument (ZetaPALS) from Brookhaven Instruments Corporation. The particles suspensions were prepared in an Eppendorf tube by diluting the original concentration of the bottle to 0.010 volume fraction adding DI water (Millipore Corp. Milli-Q system). Then 200 ml of 2.0 µm Sulfate PSL were poured together with 200 ml of 3 µm Sulfate PSL into another Eppendorf tube, mixed for 5 minutes using a VM-3000 mini vortexer bought from VWR International and placed in an ultrasonicator from VWR International (model 550T) for 15 minutes to break any possible aggregate. The same procedure was used for all other mixtures of particles.
3.2.2 Experimental

The mixture was transferred into a Pasteur pipette from VWR International (West Chester, PA) whose bottom had been previously sealed with wax. A Pasteur pipette was used instead of a capillary tube because it provides a narrow capillary in order to study the sediment and a large reservoir at the top to load a larger amount of suspension. The Pasteur pipette was mounted into a centrifuge tube BLUE MAX™ Jr. 15ml Polypropylene Conical Tubes bought from BD Falcon™ (Franklin Lakes, NJ) in order to keep the Pasteur pipette straight along its vertical axis. Then the centrifuge tube was either kept settling at normal gravity or introduced into a Sorvall® Biofuge Primo Centrifuge in order to increase the centrifugal force up to 1000 times the normal gravity (1000g). In order to recover the sediment and analyze it, the Pasteur pipette was removed from the centrifuge tube and the sediment was extracted with a needle in layers of 3 mm thickness. The layers were resuspended in DI water and placed in the ultrasonicator for 15 minutes to break any aggregates. Then particles were analyzed with a Nikon Eclipse TE2000-U inverted optical microscope with a 40× air objective.

3.2.3 Confocal Microscope Sample Preparation

60 μl of a mixture with equal volumes of 4.0 μm red fluorescent PSL (CV: 2.3%, Lot No. 646220, ζ-potential in DI water is -81.40 ± 1.21 mV) and 2.0 μm yellow-green fluorescent PSL particles (CV: 1.3%, Lot No. 21515W, ζ-potential in DI water is -52 ± 3.1 mV) bought from Interfacial Dynamics Corporation (Portland, OR) at 2% solids is placed in a rectangular capillary tube 0.20×2.0×50 mm RT3520 bought from VitroCom (Mt. Lakes, NJ). The capillary tube is sealed with optical resin and let it rest on the 2.0 mm side slightly tilted respect to the gravity vector. The particles were allowed to settle for 2 weeks. Confocal images of sediment at different
positions of the capillary were taken with an Olympus Fluoview 1000 Confocal Laser Scanning Confocal Microscope with a 60× oil objective at the Huck Institute of the Life Sciences Center for Quantitative Cell Analysis.

3.2.4 SEM Sample Preparation and Imaging

Sediments of polystyrene latex spheres can be analyzed in an SEM by using a novel fusing procedure. After the sediments had formed and reorganized, they were placed in a centrifuge at 1000 g and in the presence of 100 mM KCl for 5 minutes. The addition of salt and increased gravitational force allowed the particles in the sediment to overcome repulsive electrostatic forces, aggregating into a solid, frozen sediment. After centrifugation, the samples were removed and heated in a pressurized vessel at 120°C for 20 min. Because this temperature is above the glass transition temperature of the PSL particles, the sediments ‘fused’ into a continuous solid. This solid was extracted from the vessel / pipette, sectioned with a razor blade, and mounted for analysis in a Hitachi S-3000H Scanning Electron Microscope (SEM) at the Penn State Material Characterization Laboratory. The main benefit to this procedure is that it can show the internal structures of each layer, whereas the confocal microscopy performed (Fig. 3.3) only shows particles at the capillary wall. The lab hopes to make use of this procedure in the future to better understand the structural changes with time in our sediments.
3.3 Results and Discussion

3.3.1 Preliminary Macroscopic Observations and Results

We first saw a surprising, spontaneous layering behavior during experiments that included two different colloidal particles: green sulfate functionalized polystyrene latex (PSL) of 2.0 μm diameter and red sulfate functionalized PSL of 3.0 μm diameter. Using different colors enabled us to make quick evaluations by eye, so that we could process more samples. By using de-ionized water in equilibrium with air, we have systems with a pH of 5.6, giving a bulk double-layer thickness of roughly 200 nm. As a result, a sizable fluid layer remains between the particles, even in the sediment, allowing particle mobility and re-arrangement, in contrast to the hard sphere case\textsuperscript{13}. We examined one set of sedimenting systems that were held for 18 hours in Pasteur pipettes in de-ionized water. We discovered that the particles had spontaneously sorted by size, with the large red particles on the bottom (Fig. 3.1a&c). The experiments with PSL particles were fully reproducible with particles ranging in size from 1.0 μm to 5.0 μm.
Figure 3.1 Particle recovery of the 2.0 and 3.0 μm polystyrene latex (PSL) particle sediment and particle recovery of the 3.0 μm PSL and the 3.0 μm silica sediment (1:1 by volume initial mixture). All the scale bars at the bottom left of the different images are 10 μm. a, Mixture of 1:1 volume ratio of 2.0 μm green and 3.0 μm red sulfate-functionalized PSL particles at 0.01 volume fraction. b, Optical microscopy image (40x) of the mixture in a after dilution to $10^{-4}$ volume fraction. c, Resulting sediment of the mixture in a after sedimentation in gravity (1g) for 3 days. The white region at the bottom is wax sealing the glass capillary. d, Optical microscopy image of the green region of the sediment in c after dilution with DI water. All the particles are 2 μm green PSL. e, Optical microscopy image of the red region of the sediment in c after dilution with DI water. The image shows a mixture of 2 and 3 μm particles. f, Mixture of 1:1 volume ratio of 3 μm red sulfate-functionalized PSL and 3 μm white silica colloidal particles at 0.01 volume fraction. g, Optical microscopy image of the mixture in f after dilution to $10^{-3}$ volume fraction. h, Resulting sediment of the mixture in f after sedimentation in gravity (1g) for 3 days. The white region at the bottom is wax sealing the glass capillary. i, Optical microscopy image of the red region of the sediment in f after dilution with DI water. All the particles are 3.0 μm red PSL. j, Optical microscopy image of the white region of the sediment in f after dilution with DI water. All the particles are 3.0 μm white Silica.
Microscopic examination of the layers revealed another interesting finding. Upon extracting samples from each layer using a needle, we found that the upper region contained only 2.0 μm particles – not a single larger particle (Fig. 3.1d). However, in the lower region, which appeared macroscopically to consist entirely of the red 3.0 μm particles (Fig. 3.1c), a mixture of particles existed (Fig. 3.1e). Initially we hypothesized that this configuration could be explained by the infinite-dilution sedimentation rate, visualizing that whenever any particle reached the interface, it remained frozen in place. If this were true, then the number ratio of particles in the lower sediment region should be \( x_1/x_2 = (u_1n_1^0) / (u_2n_2^0) \), where \( u_1 \) and \( u_2 \) are the settling speeds of particles 1 and 2 respectively and \( n_1^0 \) and \( n_2^0 \) are the initial number fractions. This result was not observed for any PSL system we studied, indicating that simplistic hydrodynamic arguments do not explain our observations.

When sedimentations were repeated with particles of significantly different densities but the same size, another unusual sediment configuration resulted. A suspension having 1:1 volume ratio mixture of 3.0 μm sulfate-functionalized PSL and 3.0 μm silica particles was allowed to settle at 1g in water (Fig. 3.1f-h). After 24 hours, the sediment again consisted of two regions: an upper region composed exclusively of PSL particles (Fig. 3.1i), and a lower region composed exclusively of silica particles (Fig. 3.1j). Importantly, the same exclusive arrangement was found even with an initial mixture of 90% PSL and 10% silica by volume. If the particles had simply settled and become non-mobile in the sediment, there should certainly have been a mixture at the bottom for the 90-10 case.
3.3.2 Proposed Model for Separation: Effective Density Sorting

The precise sorting, both with the PSL / PSL and PSL / silica layering, suggests a more complex dynamic mechanism for ordering. However, the precise nature of the sorting led us to an alternative approach for predicting the composition of the sediment layers: We hypothesized that the particles were arranging so that they minimized the system’s free energy, which for our systems is dominated by the gravitational energy (i.e., density and height). That is, the sediment composition is readily explained by thermodynamics – not settling rate – for our systems. Colloidal interaction energies and entropic mixing can be neglected for the systems present in this work, since they contribute less than 1% to the total free energy.

Upon examining the gravitational potential energy for our systems, we recognized two factors: 1) individual particles have a lower effective density due to the electrical double layer around them, and 2) collectively, mixtures of particles have a higher density due to enhanced packing. Let's first examine factor 1. For a single charged sphere in an ionic liquid, the effective density is not simply the mass of the particle divided by its volume. Rather, it is the mass of the particle plus its electrical double layer (EDL), divided by the volume of the particle plus its EDL. The thickness of the EDL is a small factor times the Debye length ($\kappa^{-1}$), given by $\kappa^{-2} = \left(2n_\infty z^2 e^2 / (\varepsilon k T)\right)$. Thus, $\kappa^{-1}$ depends upon the ion concentration on the solvent ($n_\infty$), ion valence ($z$), temperature ($T$) and solution permittivity ($\varepsilon$). Universal constants in the equation are $e = 1.6022 \times 10^{-19}$ C (proton charge) and $k = 1.38065 \times 10^{-23}$ J/K (Boltzmann’s constant). The EDL will be somewhat smaller at high particle volume fractions, or it might be compressed for particles with small surface potentials or surface charge, but at low ionic strength the EDL will remain thicker relative to the particle size, lowering the effective density of the individual particles. Since the fluid in the double layer has roughly the same density as the bulk fluid, we here approximate the effective buoyant density of a single soft sphere as
\[ \rho_{\text{eff}} \approx \left( \frac{a}{a + \delta/2} \right)^3 \left[ \rho_p - \rho_f \right] + \rho_f \]  

Eq. 3.3

where \( \rho_p \) and \( \rho_f \) represent the particle and fluid densities respectively. The parameter \( \delta \) is the separation distance between spheres in a sediment, and typically, \( \kappa \delta \approx 1 \) to 5 for our systems. In cases where the particles have the same density, the larger spheres have a higher individual particle effective density (when the particles are more dense than the fluid), since the ratio of particle volume to fluid volume is higher.

The second factor, concerning the packing of two sizes of particles, is often the dominant effect. When multiple sizes of particles pack, packing densities increase. Studies have been performed to examine the random packing fractions of ellipsoids\(^{15} \), octahedra\(^{16} \), linear and cyclic chains\(^{17} \), and many other shapes\(^{16,18} \). Of particular interest to us is the finding that monodisperse spheres have a random packing fraction\(^{19} \) of \( \phi = 0.64 \), and that bi-disperse spheres\(^{20} \) can randomly pack from \( \phi = 0.64 \) up to 0.87.\(^{21} \) When a collection of spheres at a total volume fraction \( (\phi) \) exists, then the density of a packed region can be calculated as:

\[ \rho_{\text{packing}} \approx \phi y_1 \rho_1^{\text{eff}} + \phi (1 - y_1) \rho_2^{\text{eff}} + (1 - \phi) \rho_f \]  

Eq. 3.2

where \( y_1 \) represents the ratio of the volume occupied by particle 1 divided by the total volume occupied by all particles. Furthermore, \( \rho_1^{\text{eff}} \) and \( \rho_2^{\text{eff}} \) are the effective densities of the soft spheres formed by the two particles respectively, using Eq. 3.1. Because \( \phi \) is dependent on the size ratio of the two particles, mixtures of spheres have effective complex fluid densities greater than that of mono-disperse spheres. It is important to note that the effective densities of the individual particles may change \textit{within} a sediment layer (top or bottom), since larger
gravitational forces act on particles in the bottom of each layer than in the top of each layer, changing the effective separation distance ($\delta$) throughout each layer.

The governing equation for gravitational potential energy of a packed, layered sediment of bidisperse spheres combines the individual particle factor (due to the electrical double layer) and enhanced packing factor:

$$E_g = A_s g \int_0^{h_0} h \rho(h) dh \approx A_s g \left[ \int_0^{h_{bot}} h \rho_{bot} dh + \int_{h_{bot}}^{h_{top}} h \rho_{top} dh + \int_{h_{top}}^{h_0} h \rho_f dh \right]$$  \hspace{1cm} \text{Eq. 3.3}

where $A_s$ is the cross-sectional area of the sediment; $g$ is the gravitational constant; $h_0$ is the initial height of the un-settled suspension; and $h_{top}$ and $h_{bot}$ are top and bottom layer heights, respectively. With time the particles settle, and we approximate the final sediment structure as having a bottom layer, a top layer, and a fluid layer at the top. The suspension mass density varies within each layer with $h$, but since the particles plus fluid are incompressible, $h_0$ remains constant. The energy ($E$) depends upon the total sediment height ($h_0$), the system ionic strength, the configuration of the sediment layers, and the particle sizes, buoyant densities, and surface potentials. To predict the minimum-energy sediment configuration, the energy must be minimized with respect to layer composition. Because the equation has a large parameter space, it is difficult to predict quantitatively the minimum without doing the full calculation, but it can be accomplished by discretizing the layers so as to reduce the integration to a sum over all layers.

There are two important predictions given by this equation. First, when a bidisperse system of particles in a fluid has settled and reaches its minimum free energy, there will usually be two layers. These layers are generally sorted by their effective densities. Second, while sometimes the layers will be pure (like PSL / silica, which have large density differences), this equation predicts that the layers can be mixtures of particles (like PSL/ PSL). That is, we find a type of “colloidal azeotrope”, which we here call an “asederotrope”, a configuration in which a
A mixture of particles is in the minimum energy state and there is no driving force for further separation. The asederotrope composition of the two layers varies with different particle sizes, particle densities, surface potentials, and Debye lengths.

3.3.3 Comprehensive Experimental Results for Effective Density Sorting

To confirm that our minimum energy hypothesis was correct, a number of further experiments were run for two particle systems. Some systems contained particles that had the same density but different diameters, while other systems contained particles with different densities and diameters. Figure 3.2 shows the results of these studies. Figure 3.2a clearly shows both the large effect that double-layer thickness plays on the predicted asederotrope, and how different our observed configurations were from the purely hydrodynamic prediction (which trends in the opposite direction entirely). Furthermore, our data show the same trend as the model: at low radius ratios, we expect a more complete separation, with a general trend of increasing concentration of small particles in the bottom ($y_{10}$) with higher radius ratios. Our model contains no fitted parameters; it is derived using first-principles, and the only inputs for each point are the particle and solution conditions for that experiment. Deviations between our model and experimental data are in part due to sample polydispersity (~5% for each particle type), which affects the packing fractions, thus giving more small particles in the bottom. Thus, our model provides a lower bound for the data. Variations in the calculated $y_{10}$ at particular radius ratios occur because we are mapping systems with multiple parameters onto a 2-D graph; however, this graph conveys the essential concept.
Figure 3.2: Theoretical Predictions and Experimental Results for Effective Density Sorting.

a) Bidisperse polystyrene latex microspheres (sulfate-functionalized): ■ = experimental results with error bars that represent the 95% uncertainty in the repeatability for each point; — = hydrodynamic theory; ▲ = effective density model prediction. Here, particle 1 is the smaller of two PSL spheres, meaning that the x-axis is the \( \alpha_2/\alpha_1 \) and the y-axis shows the volume fraction of small spheres \( y_1 \) in the bottom layer of the sediment. The model points were calculated for each experimental point on the graph. Both the radius ratio and overall particle sizes have an effect on the final sediment composition, which is why there are two model / experimental data points given for a certain radius ratios (e.g., systems of 2.0 and 4.0 μm spheres will have the same x-value as systems of 2.5 and 5.0 μm spheres but have different y-values due to different bottom sediment configurations).

b) Polystyrene latex / poly- methylmethacrylate microspheres (sulfate functionalized): ■ = experimental results with error bars; — = hydrodynamic theory; X = effective density prediction. Here, particle 1 is the PSL, meaning that the y-axis shows the volume fraction of PSL spheres \( y_1 \) in the top layer of the sediment.
Figure 3.2b shows an additional layering phenomenon we observed, following a prediction from the minimum energy sorting model. In systems of PSL (specific gravity SG = 1.055) and PMMA (poly-methylmethacrylate) (SG = 1.19), the top layer of the sediment was always comprised of mostly or all PSL particles, even in cases when the PSL particles had a considerably higher settling rate. In contrast, the hydrodynamics of the system suggest that the top layer should be composed solely of whatever particle settles slowest. For large particle ratios, some PMMA is found in the top layer, consistent with the asederotrope predicted by our model. Although it is energetically favorable for the heavier PMMA individual particles to be at the bottom, a small number of PMMA in the top layer of the sediment enable a higher packing fraction, which reduces the overall sediment height and therefore reduces the system energy.

3.3.4 Sediment Structure and Observed Packed Particle Mobility

The results up to this point have focused on the composition of the layers, but two imaging techniques were used to confirm the sediment structure. Confocal fluorescence microscopy of a sediment was performed for a suspension of 4.0 μm red fluorescent and 2.0 μm yellow-green fluorescence sulfate PSL particles. We prepared a sample with a 1:1 volume ratio of the particles and allowed them to settle in a capillary tube slightly slanted to one side for 3 weeks. Because the particles were settled at an angle, images taken along the length of the capillary tube showed the sediment at different heights. The top of the sediment became composed exclusively of small particles (Fig 3.3a), then there was a small transition region of roughly 100 μm (Fig. 3.3b), and finally there was a lower layer with a roughly uniform composition of mixed particles (Fig 3.3c&d). These observations were confirmed using scanning electron microscopy.
Figure 3.3  Confocal microscopy images of a sediment formed by an initial mixture of 1:1 volume ratio of 4.0 μm red fluorescence and 2.0 μm yellow-green fluorescence PSL particles and evidence of particle mobility in the packed state. See description in the text. a, Top layer of the sediment composed exclusively of small particles. b, Transition zone of the sediment. c, Asederotrope proportion at the lower layers of the sediment. d, Asederotrope proportion at the bottom of the sediment. The two images in e were taken at the same point in the sediment 5 seconds apart. Notice that there is a significant amount of particle movement, especially of the small green particles, which move in and out of the focal plane. The particles with the highest mobility have been highlighted to guide the reader.
We did not observe colloidal crystallization in either layer over the course of several months, as evidenced by a lack of iridescence and confirmed by SEM (Figure 3.4), except for the top of upper layers that contained the smallest particles we used (1.4 μm diameter). Even though certain samples were settled with Peclet numbers (Pe = Ua/D, where U is sedimentation velocity, a is particle radius, and D is particle diffusion coefficient) smaller than 0.1, the bidispersity of our sediments and polydispersities of our individual particles made crystallization impossible on the timescales used in our experiments.

Figure 3.4. Structure of bidisperse packed particle sediments: 1.7 and 2.5 μm sulfate-functionalized PSL. Details of fixing the particles for electron microscopy imaging can be found in the section “SEM Analysis of Packed Sediments” in the Supplementary Discussion. a) Top region of sediment. b) Transition region of sediment. c) Upper part of bottom region of sediment. d) Lower part of bottom region of sediment. Note the lack of crystallization of the particles in both the top and bottom regions of the sediment, and the sharpness of the transition region in b).
While we have not evaluated our detailed transport dynamics with Stokesian Dynamics\textsuperscript{22} or other simulations, we expect that the soft sphere state of our particles enables our sediment layering. It has been shown that for packed hard-sphere colloidal sediments, particle diffusion coefficients are effectively zero.\textsuperscript{13} However, for interacting, repulsive spheres, we expect that particles can still inter-diffuse at lower ionic strength,\textsuperscript{23,24} and we observe this in our experiments (Fig. 3.3e). We expect that particles with larger-magnitude surface potentials will remain mobile at higher packing fractions due to their increased repulsion. Non-zero diffusion coefficients allow for our sediments to rearrange themselves into the predicted thermodynamically favorable configuration. We directly observed dense-packed re-arrangement in the PSL-PMMA samples (Fig 3.2b). The larger PSL settled much faster than the PMMA. The sediment was initially mixed, but after 3 days, most or all of the PMMA had migrated to the bottom of the sediment. If our particles had been glassy, rather than showing mobility as seen in Fig. 3e, this re-arrangement would not occur, and the particles would have frozen into a non-equilibrium configuration, such as the amorphous, glassy sediments previously observed.\textsuperscript{13}

We note that since the layering phenomena described in this paper requires mobile particles in the sediment, our phenomenon is different from the Brazil nut phenomenon. A comparison to the Brazil nut phenomenon\textsuperscript{25}, especially a comparison with objects greater than 1 mm settling in air, requires two points to be considered. First, the BNP does not typically use a “true temperature”, but a biased temperature.\textsuperscript{26} This occurs because while the particles are moved up at an arbitrary speed during shaking, depending upon the lift rate, they fall at roughly gravitational acceleration. Second, since the particles settle in air at high Reynolds numbers, they accelerate at roughly the same rate; in contrast, in our colloidal systems the particles settle at terminal velocity, so that small particles settle more slowly than larger ones.
Usually, when the particles start as a mixture and are centrifuged at 1000g, they sort into the expected minimum energy configuration, but this is not always the case. The importance of packed particle mobility can be examined by immobilizing a sediment using centrifugation. In one experiment we settled 2.0 μm blue PSL particles at 1 g, and then we settled 3.0 m green PSL
particles at 1g on top. With time the particles began to re-arrange into the expected minimum-energy configuration. However, when this same experiment was run at 1000g, the particles did not invert (Figure 3.5). In the 1000g case, the gravitational forces overcame the colloidal repulsion, causing the particles to aggregate irreversibly and stop diffusing. This freezing effect has been used to measure maximum repulsive colloidal forces.\textsuperscript{27,28}

### 3.4 Conclusions

Traditionally, characterization of particle sediments has relied primarily on a single dimensionless quantity: the Peclet number (Pe). By comparing the rate of particle sedimentation to that of particle diffusion, sediments could be predicted to form glassy sediments (where sedimentation dominates, high Pe) or colloidal crystals (where diffusion dominates, low Pe). In this work, we observed a third type of sediment, mobile layered sediments. Knowing the Peclet number alone does not enable us to predict this phenomenon. Instead, we propose two essential conditions that must be met to form layered sediments: 1) the particles must settle fast enough to prevent crystallization, but 2) must remain mobile once settled. Condition (1) typically requires $\text{Pe} > 0.01$ (i.e., faster settling), but can also be met for bidisperse / polydisperse samples with lower Peclet numbers (where crystallization can be hindered or made impossible by the particle inhomogeneity). Second, particle mobility also requires that the repulsive forces between particles be sufficient to prevent direct contact of the particles, since hard sphere repulsions do not allow for sufficient mobility, especially for large particles.\textsuperscript{7,13} It is interesting to note that in our systems, having $1/\kappa a$ from 0.008 to 0.45 is sufficient to provide particle mobility. We note that these conditions for particle mobility are frequently met in aqueous systems where the particles are highly-charged, and so our systems represent a common case. We expect that in the
future we will be able to plot a phase diagram showing the traditional crystallization, glassy sedimentation, and mobile asederotrope regions. The diagram would have as one axis the time of sedimentation divided by the time of crystallization (perhaps the system Peclet number), and as another axis $1/\kappa a$ or a similar measure of particle interaction range.

![Image](image.png)

**Figure 3.6: Layers of sorted particles.** 
**a,** Original mixture of 150 nm gold, 3.0 μm white Silica, 3.0 μm red Sulfate PSL, 2.0 μm green Sulfate PSL and 0.99 μm Sulfate PSL at 0.01 volume fraction. 
**b,** Front view of the 5 layer cake after centrifugation at 1000g for 30 minutes, with the gold on the bottom; the particles layer according to the order given in (a). The white region at the bottom is wax sealing the glass capillary.  
**c,** Back view of the 5 layer cake after centrifugation at 1000g for 30 minutes.

In principle the minimization of energy should enable us to predict final sediment layer compositions for any multi-component mixture of particles in which the particles remain mobile. Indeed, we performed one experiment with 5 different particles at 1000g, each having a different size or density, and we obtained a reasonable sorting for all of these, almost like a fractionating distillation column (Fig. 3.6). On the other hand, few results exist — either from modeling or experiments — for the packing fractions of multi-component mixtures of spherical particles$^{20}$, and
even less so for mixtures of say singlet and doublet particles. Such studies require great care. It is possible that such mixed packing fractions might be measurable by using the predictions from this work.

3.5 Acknowledgements and Permissions

Chapter 3 is a modified version of the author’s publication:

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I would like to thank César González Serrano and Darrell Velegol for pulling me (kicking and screaming at first) into this fascinating work. Cesar originated the work and conducted the preliminary experiments, while my role began primarily as a theoretical consultant. Over time, we began to work together on both the experimental and modeling results. After Cesar departed from the Velegol lab, I headed up the final experimental results (Fig 3.2, Fig 3.4) and worked collaboratively with Darrell and Cesar to finalize our model for publication, writing a considerable portion of the manuscript, of which I am a corresponding author.
3.6 References


21 McGeary, R.K., Mechanical Packing of Spherical Particles Vibratory Compacting: Principles and Methods (Plenum Press, New York, 1967). See Fig. 3 on p. 220, which shows the packing fractions, with data that support the calculations in Ref. 19.


28 Bensley, C. N., Hunter, R. J. The coagulation of concentrated colloidal dispersions at low electrolyte concentrations II. Experimental coagulation pressures. J. Colloid Interface Sci. 1983, 92, 448-462.
Chapter 4

Simple Fabrication of Gold-Silver Heterodoublet Motors

4.1 Introduction & Background

4.1.1 Introduction

Metallic colloidal doublets have a number of potential applications, including sensing, colloidal robotics, colloidal antennae, and surface-enhanced Raman spectroscopy. The point contact of two metallic spheres has a region around it where the surfaces are nearly touching, which enables the exploitation of surface plasmon resonance in that region, or in the case of different metals, even a slight diode function. The purpose of this chapter is to describe a simple and inexpensive method for fabricating metallic homodoublets or heterodoublets (and even triplets), with electrical connectivity between the two spheres in the doublet. We demonstrate gold–gold, silver–silver, and gold–silver doublets of roughly micrometer size.

4.1.2 Literature Review

Homodoublets and heterodoublets of colloidal particles have been previously synthesized using a variety of techniques. Most work in the field has been done using polymeric or metal-oxide colloids. The most common technique for the production of colloidal doublets has been templating, in which a glass or silicon substrate is chemically patterned, typically using a photoresist, creating a series of pits. These pits allow for specific assemblies of particles, based on for instance the size of both the particles and the templates. These studies have been
performed generally on only polymer and silica colloids with sizes on the scale of 500–1000 nm. Silica doublets (with sphere diameters ranging from 174 nm to 2.3 μm) have been formed from shear-induced aggregation using ammonia and ethanol to cause destabilization in solution. Additionally, doublets of silica particles (with sphere diameters on the order of 300 nm) were formed by adding tetraethylorthosilicate to a suspension of silica colloids. The tetraethylorthosilicate condenses on the silica surface, ‘fixing' aggregated silica doublets in place. A heat-assisted convective assembly technique was used to produce ZnS or polystyrene doublets; in this technique, the temperature is raised to increase Brownian motion (and possibly buoyant convection) and then cooled to reduce the motion. Binary colloidal structures of polystyrene have also been assembled by functionalizing two different sizes of polystyrene colloid (0.94 and 5.5 μm, respectively) with interacting proteins that biomolecularly cross-link the colloids together. Finally, clusters of silica, polystyrene, or polymethylmethacrylate on the order of a micrometer were formed by the slow evaporation of an organic solvent in water and in the presence of a stabilizing block copolymer.

The synthesis of doublets of metallic colloids has also been accomplished through a variety of methods. Gold nanoparticles of size 150 nm have been deposited next to each other on a substrate using electron beam lithography. Similarly, simple gold aggregates can be grown in 2-D arrays on organosilane-coated substrates. Gold–iron oxide nanoparticle doublets have been synthesized by decomposition of Fe(CO)₅ on the surfaces of gold nanoparticles, while silver–iron oxide nanoparticle doublets were formed by the reduction of silver on the surface of iron oxide nanoparticles. Likewise, a method of forming silver–iron oxide nanoparticle doublets by nucleating a silver nanoparticle on a Fe₃O₄ nanoparticle at a liquid–liquid interface has been described. Doublets of 1.4 nm colloidal gold were prepared by attaching the nanoparticles to single-stranded DNA oligonucleotides and assembled by adding the complementary DNA template to solution. Asymmetric doublets of spherical oxide particles and gold half-shells were
formed by coating an array of 600 nm oxide particles with a thin gold film, which dewetted into half-shells after thermal annealing.\textsuperscript{23}

In addition to traditional doublets, the formation of structures similar to metallic heterodoublets, yet lacking two distinct particles, has also been accomplished. A typical example is the synthesis of gold–platinum nanorods by vapor deposition and electroplating of the two metals on an alumina membrane.\textsuperscript{24} Gold–silica–gold nanodisks have been formed by electron beam lithography and evaporation onto quartz substrates.\textsuperscript{25} Silica spheres were capped with gold and titanium through a patterning procedure involving the e-beam sputtering of the metals onto the silica spheres, which were partially obscured by a photoresist blocking film.\textsuperscript{26} Cobalt–palladium nano-‗acorns‘ (showing clear phase separation) were produced when precursor cobalt and palladium complexes were reduced in di-\textit{n}-octyl ether and in the presence of 1-octadecanethiol.\textsuperscript{27}

\textbf{4.1.3 Chapter Aims & Overview}

Two challenges with most of the previously mentioned techniques for fabricating doublets are that they either (a) are limited to particular materials (e.g., polymers or oxides or metals) or (b) are difficult to scale up in production. Recently, a robust technique for fabricating colloidal doublets has been published by our group. The salting out/quenching/fusing (SQF) technique\textsuperscript{28} uses the reliance of colloidal stability in aqueous solutions on the ionic strength (or other stimulus, such as pH) of that solution. By increasing the ionic strength greatly, a suspension of colloidal particles will usually aggregate in a diffusion-limited manner due to the increased ionic shielding of electrostatic repulsive forces. Particles that aggregate are held together by their attractive van der Waals forces. We then halt aggregation by diluting the ionic strength, thus restoring stability due to restored electrostatic repulsion. The solution of aggregates is usually quenched early enough in the aggregation process to yield primarily doublets and unreacted
singlets in solution, although sometimes it is desirable to also form a fraction of triplets, which we test in the present research. Finally, in order to better stabilize the doublets after aggregation and quenching, a fusing step is often added in which polymer particles are brought above their glass transition temperature, allowing doublets to fuse together. Previously, the SQF technique was performed on polymer colloids and silica colloids. The primary advantages of the SQF technique are simplicity (requiring few steps, few materials, and little time) and flexibility (allowing for a wide range of degrees of aggregation and allowing for the use of mixed materials).

In the present research, we combine the salting out and quenching steps described above with known techniques for synthesizing micrometer size metal particles in order to fabricate gold–gold, silver–silver, or gold–silver doublets. The advances relative to our previous doublet fabrication were several for the metal doublets. (1) For polymer–polymer or polymer–silica doublets, the mechanical stability is greatly enhanced by fusing the doublet above the glass transition temperature of the polymer. With their high melting points, the fusing step is not feasible for our metal–metal doublets; however, we hypothesized that since the metals have such high Hamaker constants in aqueous solution, that attractive van der Waals forces might maintain the mechanical integrity of the doublets. Thus, we conducted analyses of mechanical stability (with sonication) to determine the fraction of doublets that remained as doublets. (2) Many of the interesting and important properties of metallic colloidal doublets require that the spheres in the doublet have electrical connectivity. However, measuring the connectivity of these doublets is a significant challenge. Recently, it has been shown that heterogeneous nanorods synthesized from gold and platinum in hydrogen peroxide solutions show a movement that is 10× or more faster than the movement predicted by Brownian motion alone over 10 s or more. This movement, which works by autoelectrophoresis resulting from the electrochemical decomposition of H₂O₂, requires electrical connectivity of the two metals across their interface.
This process is discussed in more detail in Chapter 5. Here we use this result *analytically* to test gold−silver heterodoublets for electrical connectivity. Our findings open the door to detailed studies of electron transport between the spheres in the doublet. (3) A more advanced colloidal assembly that can be fabricated using the SQ process is a triplet of particles. Also, it is sometimes useful (or required) to form doublets at a rate less than the rapid aggregation rate. In this research, we demonstrate practically that the SQF (or SQ) process is readily generalized to operate at slower rates, and to form triplets of particles.

4.2 Experimental Methods & Materials

4.2.1 Materials

To synthesize the gold particles, HAuCl₄ was purchased from Strem Chemicals (lot no. B7817045). For the silver particles, AgNO₃ was purchased from Sigma (lot no. 124K3640). In both cases, reduction of the metal ions was done by l-ascorbic acid (C₆H₈O₆, Sigma, lot no. 07908BD). The steric stabilizer used in both syntheses was gum arabic, a blend of galactose, rhamnose, arabinose, and glucuronic acid, with a molecular weight around 250 000 (Sigma). Solutions of KCl (EM Science, lot no. PX14051) were used in the aggregation steps. Deionized (DI) water used in all aqueous solutions came from a Millipore Corporation MilliQ system, with specific resistance greater than 1 MΩ cm (due to equilibration with CO₂ in air).
4.2.2 Gold and Silver Colloid Synthesis and Characterization

A robust technique for the synthesis of micrometer-scale colloidal metal particles has been previously described in detail for both gold and silver.\textsuperscript{33,34,35} In this technique, gold or silver ions are reduced in solution with gum arabic over 1–2 days. The resulting metal nanoparticles are initially solvated but eventually drop out of solution, forming seed particles. These seed particles grow over time as the reduction reaction continues, until large particles formed by the clustering of nanoparticles remain. The gum arabic acts as a steric stabilizer, preventing aggregation of these larger particles due to the high ionic strength of the reaction solutions.

For the synthesis of the colloidal gold, two 75 mL solutions were prepared. The first contained 25 mM HAuCl\textsubscript{4} and 3 wt % gum arabic. The second contained 50 mM l-ascorbic acid and 3 wt % gum arabic. The solutions were combined in a 250 mL covered reaction flask and stirred rapidly for 48 h. After stirring, the newly formed gold particles were allowed to settle for 3 h. The supernatant was drawn off, and the gold particles were rinsed twice and finally resuspended in DI water.

The colloidal silver was formed using a similar procedure. Again, two 75 mL solutions were prepared. The first contained 167 mM silver nitrate and 7 wt % gum arabic. The second contained 333 mM l-ascorbic acid and 7 wt % gum arabic. The solutions were again combined in a 250 mL covered reaction flask and stirred for 48 h. The resulting silver particles were settled for 3 h, rinsed twice, and resuspended in DI water.

The particles were imaged and sized using a JEOL 6700F field emission scanning electron microscope (FESEM) with accelerating voltages of 3 and 5 keV and an operating current of 20 μA, allowing for magnifications from 1300 to 150 000×. Optical images were taken using a Nikon Eclipse TE2000-U inverted optical microscope with magnifications of 20, 40, and 100×. Zeta potentials of the particles were measured with a Brookhaven Instruments PALS (phase
analysis light scattering) instrument, at ionic concentrations of 1 and 100 mM KCl. The gold particles were 0.7−1.3 μm in diameter, while the silver particles were 0.5−1.5 μm in diameter. For the zeta potentials at 1 mM KCl, ζ_{Au} = −50 mV and ζ_{Ag} = −58 mV, while at 100 mM we found that ζ_{Au} = −21 mV and ζ_{Ag} = −27 mV. Figure 4.1 shows the particles imaged under the FESEM.

\[ \text{Figure 4.1 FESEM images of synthesized metallic colloids. (a) Gold and (b) silver. The scale bar at the bottom right of the images is 1 μm. Note that the gold particles are typically smoother than the silver particles.} \]

4.2.3 Doublet Formation and Purification

Doublets were formed from the metallic colloids by using the salting out–quenching (SQ) technique described earlier. Because using higher volume fractions of particles in solution reduces the aggregation time, gold and silver stock solutions were created by concentrating the gold and silver solutions by centrifugation to volume fractions of 0.028 for gold and 0.065 for silver. All aggregation was performed in glass centrifuge tubes to minimize the amount of particles sticking to the walls of the aggregation vessel. Aggregation conditions were achieved by adding an equal amount of 2.5 M KCl solution to the solution containing the desired colloidal particles. Solutions were allowed to aggregate for an experimentally determined amount of time.
and were mixed by vortexing the solution every minute to prevent particle settling. Solutions were quenched after the appropriate time to halt aggregation. Due to the presence of leftover steric stabilizer from the reaction step, the appropriate aggregation time was always longer than the Smoluchowski rapid flocculation time. As a result, trial-and-error was used to find an appropriate time for each system. See Table 4.1 for a list of final parameters of each separate aggregation solution conditions. After quenching, the resulting doublet solutions were studied statistically through optical microscopy to determine yields of singlets, doublets, and larger aggregates.

To purify these solutions to increase doublet yield, qualitative separations were performed using sucrose gradients in gravity. Linear sucrose gradients of height 10 cm were prepared using sucrose concentrations that yielded specific gravities of 1.02 and 1.36 for the top and bottom, respectively. Both sucrose solutions had adjusted ionic concentrations of 10 mM KCl. Approximately 1 mL of gold and silver aggregate solutions with adjusted volume fractions on the order of $10^{-4}$ were loaded on top of the gradient and allowed to separate. After a separation time on the order of 45 min, 1 mL aliquots of the particles in the gradient were taken, reconcentrated, and imaged. Imaging of these purified particles was done both optically and using FESEM and can be found in the next section.

**Table 4.1:** Aggregation Conditions for SQ Metallic Doublet Formation

<table>
<thead>
<tr>
<th></th>
<th>gold stock volume</th>
<th>silver stock volume</th>
<th>2.5 M KCl volume</th>
<th>aggregation time</th>
<th>volume DI to quench</th>
</tr>
</thead>
<tbody>
<tr>
<td>gold—gold</td>
<td>40 μL</td>
<td>0 μL</td>
<td>40 μL</td>
<td>20 min</td>
<td>5 mL</td>
</tr>
<tr>
<td>silver—silver</td>
<td>0 μL</td>
<td>40 μL</td>
<td>40 μL</td>
<td>10 min</td>
<td>5 mL</td>
</tr>
<tr>
<td>gold—silver</td>
<td>25 μL</td>
<td>15 μL</td>
<td>40 μL</td>
<td>15 min</td>
<td>5 mL</td>
</tr>
</tbody>
</table>
4.2.4 Electrical Connectivity of Doublets

To test for electrical connectivity, the doublets were observed in a 3% hydrogen peroxide solution under an optical microscope at 20× magnification. The H₂O₂ solution was first placed in a Petri dish, and 8 μL of the doublet solutions (after quenching) was added. The movement of the doublets was observed and recorded. When the two spheres of the doublet are electrically connected, a spontaneous autoelectrophoresis occurs. This technique has only recently been developed and does not yet give quantitative information about conductivity but is used for qualitative analytical purposes to examine electrical connectivity.⁴,⁵ Previous literature has shown that if no electrical connectivity exists between the gold and silver, no autoelectrophoresis of the particle occurs.⁴,⁵,32

4.2.5 Stability of Doublets Under Sonication

Sonication of colloidal aggregates is a simple and effective test of the aggregates' mechanical stability. It has been used in previous studies of the SQF technique as a way to break apart unstable doublets.²⁸ For the metallic doublet solutions, a sample of each was sonicated for 30 min and its composition of aggregates was statistically analyzed again through optical microscopy. Sonication was performed using a VWR International ultrasonicator (model 550T).
4.3 Results & Discussion

4.3.1 Doublet Formation and Aggregate Distribution

Metallic doublets form readily under the conditions described previously, and they remain stable both in solution (i.e., do not aggregate) and in sonication (i.e., doublets do not split back into singlets). Figure 4.2 shows FESEM images of the doublets. A key question concerns the fraction of the particles that become doublets or triplets or other aggregates. Figure 4.3 shows statistics of the SQF procedure for forming metallic doublets, as well as the stability results for each system as tested through sonication. Figure 4.4 shows doublets that have been purified using the density gradient sedimentation technique. After fabricating aggregates of various size using the quick and inexpensive SQ process, we are readily able to separate aggregates of various size, as has been done previously in the literature for more complex assemblies.36
Due to the high ionic concentrations necessary for synthesis of the original particles, it is not surprising to find a small number of doublets and larger aggregates in the initial stock suspensions of gold and silver singlets. However, through the SQ technique, yield of these doublets is increased to about 20% for the single metal systems and to about 28% for the gold–silver system. Figure 4.2 shows FESEM images of the doublets. Of particular interest is the contrast between Figure 4.2c and Figure 4.2d, which clearly shows that gold–silver, gold–gold, and silver–silver doublets are all present in the mixed-metal solution. Measurements of the zeta potentials of the gold–gold and silver–silver doublets revealed no statistical change from the singlet systems. The zeta potential of the gold–silver particles was found to be −59 mV after quenching (at 2 mM KCl) and −24 mV in 100 mM KCl.

Figure 4.2: FESEM images of synthesized metallic colloidal doublets. (a) gold–gold from the gold-only solution, (b) silver–silver from the silver-only solution, (c) gold–silver from the gold–silver solution, and (d) gold–gold and silver–silver from the gold–silver solution images.
The Smoluchowski rapid flocculation time provides a characteristic time for the singlets to aggregate into doublets. This time (τ) is given by \( \tau = \pi \eta a^3 / 2kT \phi \) for a system of spherical colloids, where \( \eta \) is the viscosity of the solution (0.0010 Pa·s for aqueous solutions at 293 K), \( 2a \) is the diameter of the particles (roughly 1 μm for our particles), and \( \phi \) is the volume fraction of
particles in solution. For our metallic systems, \( \tau \) would be on the order of seconds at high ionic strength. However, we did not see any significant aggregation on this time scale. The delay is explained by the presence of sterically stabilizing gum arabic that is leftover from the synthesis of each metallic colloid. Significant aggregation was not seen for any of the three systems until a time of 10 min. This suggests that the stability ratio for these colloidal systems is on the order of 500, even at a very high ionic strength of 1.25 M.

Although the presence of a sterically stabilizing polymer was originally not a desirable facet of the SQ experiment, the experiments do show a useful consequence. For systems that are difficult to control - for example, nanoparticles often have rapid aggregation times of less than a microsecond - we simply manipulate the stability ratio to allow aggregation at slower rates, giving more control over the state of the system when quenched. By drawing out the aggregation, it becomes possible to freeze the system in a more precise configuration. This result is a simple consequence of colloidal stability theory, and we have demonstrated it experimentally.

**4.3.2 Doublet Purification**

Purification of the doublets was achieved using density gradient separation, as described earlier. As shown in Figure 4.4, gold singlets (a), doublets (b), triplets (c), and \( n \)-aggregates with \( 3 \leq n \leq 5 \) (d) were all successfully purified to a purity of 85% or greater. Of particular interest are the separated triplets. While it is reasonable to expect the singlets and doublets to separate out from the larger aggregates, it is promising to see a layer of fairly pure triplets as well. This separations behavior, combined with the control granted by the presence of a steric stabilizer, shows that it would be possible to use the SQ technique to assemble and purify a high yield of colloidal triplets in addition to the doublets shown here. We envision instances where having a
quick and cheap method for fabricating triplets would be quite useful, especially if the precise final structure were less important than simply having three particles together.

4.3.3 Doublet and Aggregate Stability

The homodoublet suspensions of gold–gold and silver–silver were found to be mechanically stable since the relative concentrations of singles, doublets, and larger aggregates were practically unchanged after sonication (save for some small breakup of the larger

Figure 4.4: Optical images of purified gold aggregates.

(a) Purified gold singlets, 20× magnification, roughly 90% purity. (b) Purified gold doublets at 20×, roughly 85% purity. (c) Purified triplets at 20×, roughly 85% purity. (d) Purified small aggregates at 40×, with a fairly narrow size distribution. We note that the clarity of the images is diminished due to the presence of the sucrose. Nevertheless, singlets, doublets, triplets, and higher aggregates are still discernible.
aggregates). In the heterodoublet gold–silver solution, significant breakup was seen of both the doublets and the larger aggregates. The homodoublet stability is readily explained by the large Hamaker constants \((A)\) that govern attractive van der Waals forces for gold–water–gold \((A \approx 90 \text{ kT})\) and silver–water–silver \((A \approx 100 \text{ kT})\) systems,\(^{29}\) between 1 and 2 orders of magnitude higher than most polymers or ceramics in water. The breakup of the silver–gold heterodoublets after 30 min of sonication is not so readily explained, at least with our current techniques. However, we note that no significant change in the aggregation percentages of any of the unsonicated solutions was seen over the course of 4 months. This suggests that both the gold and silver are mechanically stable and that doublets of the gold, silver, and gold–silver do not break up over time. Additionally, qualitative studies have been performed suggesting that all types of the doublets can withstand low-to-moderate shear forces, as well as shorter sonication times of a few minutes.

### 4.3.4 Motility of Gold-Silver Doublets

In the testing of doublets for electrical connectivity, only a small amount of Brownian motion was detected when the gold–gold or silver–silver homodoublet systems were placed in \(\text{H}_2\text{O}_2\) aqueous solution. On the other hand, for the gold–silver suspension, significant movement of many doublets (and larger aggregates) was seen at speeds much faster than given by Brownian motion. A time-lapse image of one typical set of particles is shown in Figure 4.5. Particles were observed moving at speeds between 2 and 15 \(\mu\text{m}/\text{s}\), depending on size and number of aggregates, and were often seen moving in circles, or in some cases, rotating quickly in one direction while otherwise staying in place. In one especially interesting case, a doublet moved quickly due to the autoelectrophoresis, and for an unknown reason broke during its movement (Figure 4.6). The
rapid movement ceased immediately, and the two resulting singlets showed only Brownian motion.

Figure 4.5: Optical time lapse image (20×) of gold–silver and other doublets and aggregates moving in a 3% hydrogen peroxide solution. Approximate time between frames is 1/8 s.

Figure 4.6: Optical time lapse image (20×) of gold–silver doublet (indicated inside circle) before (a) and after (b) breakup of the two component particles in 1% peroxide. Scale bar is 20 μm. Approximate time between frames is 1/2 s, total elapsed time in each panel is 3 s. Before breakup, the doublet moves in a directed circle. After breakup, there is no significant non-Brownian movement of either gold or silver particle.
4.4 Conclusions

We have shown the ability to fabricate purified gold–gold, silver–silver, and gold–silver doublets of micrometer size. The doublets are held together mechanically by van der Waals forces. In addition, we have shown that the silver–gold heterodoublets are electrically connected, as they show electrokinetic movement in hydrogen peroxide solution very similar to the movement of heterogeneous metallic nanorods.

We note that the fabrication method might seem to be simple - and indeed it is. Once the proper conditions of ionic strength and quenching time are established, the doublets can be fabricated in less time than it takes to read this chapter. We have established in this research that the metal doublets remain stable in suspension, even to sonication over several minutes. The combining of several techniques of particle synthesis, including the analysis using the electrokinetic motor concept, has yielded a particular type of doublet that could be especially useful in sensing, electronics, colloidal robotics, or colloidal antennae. The next step is to integrate other materials into these systems and to examine the behavior of the resulting motors.

4.5 Acknowledgements and Permissions

Chapter 4 is a modified version of the author’s publication:

4.6 References


31 Prieve, D. C.; Gerhart, H. L.; Smith, R.E. *Ind. Eng. Chem. Prod. Res. Dev.*, **1978**, 17, 32. One difference between the technique in the Prieve paper and the technique in the present research is that the source of ions producing the electric field is from a surrounding “fuel” (H₂O₂), and the particle catalyzes the decomposition to give the ions. See also a patent referenced in the Prieve paper, U.S. Patent 3,585,084 (Lester Steinbrecher, issued 1971).


Chapter 5

Colloidal Trimers Fabricated Through Quenched Electrostatic Assembly

5.1 Introduction & Background

5.1.1 Introduction

As the designs for colloidal assemblies become more sophisticated, they will increasingly require multiple component particles, sometimes placed in a particular order. The ability to create complex, ordered assemblies will allow for the creation of functional colloidal devices. For example, when a gold and a silver sphere are assembled together into a doublet and that doublet is placed in an aqueous solution of hydrogen peroxide, the resulting assembly acts as a catalytic motor, moving about rapidly in solution. One way to increase the complexity of these motor assemblies would be the addition of a third “switch” particle – a particle that enables externally controllable on/off manipulation of the motor. This switch particle would be placed between the gold and silver particles, such that this “trimer” assembly (trimer here denotes three distinct precursor particles assembled into one stable assembly) has the particle order of gold-switch-silver. Although the particle material components and their order of placement are thus constrained, the precise orientation of the assembly – whether the “bond angle” of the three particles is 90 or 180 or 137 degrees – is less important. The question we tackle in this section is how to assemble such a device, which 1) is composed of up to three different materials, 2) has a particular sequence (1-2-3 or 2-1-3 or 2-3-1), and 3) possesses sufficient mechanical stability that it remains assembled.
5.1.2 Literature Review

Before describing the assembly method introduced in this section – we call it “Quenched Electrostatic Assembly” (QEA) – we look at what has come before. In short, we have not been able to identify any instances of colloidal trimers made from three different colloidal components in the literature. There are numerous techniques described for assembling two colloidal particles together,\textsuperscript{5,6,7,8,9,10,11,12} and perhaps several of these have the capability to assemble three different materials. Specifically, both template-directed assembly in physical templates\textsuperscript{9,13}, and in “templates” formed using acoustic traps\textsuperscript{14} or solution micelles\textsuperscript{15}, and “patchy” particle assembly, utilizing one, two, or more regions of differing particle surface functionality\textsuperscript{10,16,17,18}, could potentially be used to form three-component assemblies. The biggest drawback to these techniques is that any path to scaled-up production would be difficult and costly. Other techniques, such as multistep seeded polymerization\textsuperscript{19,20} and particle “buckling”\textsuperscript{8,21} exist to give colloidal particles the necessary shape morphology for multicomponent assembly, but are limited to specific materials.

5.1.3 Chapter Aims & Overview

Here we make an important advance on a technique previously-used in our lab, the stimulate-quench-fuse (SQF) method, that makes the method capable of producing colloidal trimers.\textsuperscript{2,7,22} In our past work, we have used the SQF method to produce low-order colloidal aggregates, especially homo- and heterodoublets. While the SQF technique is not material-specific, it has had difficulty in producing colloidal trimers in which the three components have a particular sequence. By modifying the SQF method, we have developed a technique for the controlled aggregation of multiple colloidal particles: Quenched Electrostatic Assembly (QEA).
The QEA technique builds on the SQF technique, providing a general assembly technique for producing heterodoublets, trimers, and higher-order aggregates of two or more distinct, charged colloidal particles. In the QEA method, larger “core” particles and smaller, oppositely-charged “satellite” particles are allowed to aggregate in solution. But whereas the quenching might be done by diluting the solution ionic strength with SQF, here the quenching step uses the addition of charged nanoparticles to coat the core particle. The nanoparticles thus make both the cores and the satellites have the same sign of charge, halting further aggregation with electrostatic repulsion. Since the nanoparticles have a large diffusion coefficient and a high number density, when they are added to the solution, they adhere to the core particles very quickly, typically within a few seconds, quenching the aggregation.

The nanoparticles also serve another important function. After fabricating our assemblies, we want them to maintain mechanical integrity. During processing steps involving sonication or high shear rates, or at some point during transport or shipping, the particles will encounter mechanical stresses that can break them apart. In non-polymeric systems, we must rely on van der Waals attractive forces to keep particles assembled, which works fairly well for metals with high Hamaker constants but not for many other materials. We promote the mechanical stability of our assemblies by bringing the polymeric nanoparticle quench coating above its glass transition temperature ($T_g$) for an appropriate time, allowing the particles to “fuse” into one another. In this section, we show that the QEA technique leads to stability in both the colloidal aggregation and mechanical integrity senses.
5.2 Experimental Methods & Materials

5.2.1 Materials

Monodisperse 3.3 µm amidine functionalized polystyrene latex (PSL) microspheres (4.1% w/v), monodisperse 0.81 µm sulfate-functionalized polystyrene latex microspheres (8.1% w/v) and monodisperse 20 nm sulfate-functionalized fluorescent polystyrene latex microspheres (2% w/v) were purchased from Interfacial Dynamics Corporation (Portland, OR). Monodisperse 3.01 µm (9.8% w/v) silica microspheres were purchased from Bang’s Laboratories (Fishers, IN). Undoped silicon metal powder with a purity of 99.999% was purchased from Atlantic Equipment Engineers (NJ). Gold and Silver microparticles were synthesized using the recipe developed by Goia and Matijevic\(^{24}\) and modified by Velikov\(^{25}\). The cationic polyelectrolyte poly(allylamine hydrochloride) (PAH, Mw 70,000), silver nitrate for colloidal silver synthesis, L-ascorbic acid (C\(_6\)H\(_8\)O\(_6\)), gum Arabic and potassium chloride (KCl) were purchased from Sigma-Aldrich Chemicals, USA. To synthesize the gold particles, gold chloride (HAuCl\(_4\)) was purchased from Strem Chemicals. Deionized (DI) water used in all aqueous solutions came from a Millipore Corporation MilliQ system, with specific resistance greater than 1 MΩ.cm (due to equilibration with CO\(_2\) in air). Hydrogen peroxide, filter papers, and glassware were obtained from VWR International.

5.2.2 Instrumentation

The optical microscopy images were obtained on a Nikon Eclipse TE2000-U inverted optical microscope. The electron microscopy images were obtained on a Hitachi S-3000H Scanning Electron Microscope (SEM) at the Penn State Material Characterization Laboratory.
The confocal and DIC optical microscopy images were captured using an Olympus Fluoview 1000 laser scanning confocal microscope (Olympus America Inc, Melville, NY) at the Huck Institute of the Life Sciences Center for Quantitative Cell Analysis. The Sorvall Biofuge Primo Centrifuge was from Kendro Laboratory Products, and it was equipped with a swing-bucket rotor. The Ultrasonicator was from VWR International (model 550T). The heat treatments took place in an autoclave oven set to 120 °C.

5.2.3 Silicon Microparticle Preparation:

Undoped silicon powder was ground in a mortar and pestle in the presence of DI water. The resulting crushed particle slurry was suspended in 50 mL DI water in test tubes and allowed to stand under gravity for 17 hours after which the top 45 mL of the supernatant (containing smaller silicon particles) was drawn off. We repeat this step to clear most of the smaller than desired silicon particles from solution. The remaining suspension of silicon was filtered through an 8 µm filter; the residue containing bigger silicon particles was discarded and the filtrate containing mostly 1-8 µm silicon particles was collected.

5.2.4 Synthesis of Gold and Silver Particles:

Silver (Ag) and Gold (Au) microparticles were synthesized using the recipe developed by Goia and Matijevic24 and modified by Velikov25, involving the reduction of metal ions to metallic silver and gold by ascorbic acid, as described in Section 4.2.2. The diameter of the silver particles ranged from 0.5 µm to 1.5 µm. The diameter of the gold particles ranged from 0.7 µm to 1.3 µm. The silver and gold particle suspensions, with volume fractions as synthesized of 0.0005 and 0.00016 respectively, were used in all later assembly experiments.
5.2.5 Functionalization of Silicon and Silica Particles with a Positively-Charged Polyelectrolyte.

Silicon and silica particles were made positively charged by coating them with a positively charged polyelectrolyte, PAH. 40 mL of 20 µM of PAH solution was prepared in 30 mM KCl and 20 mL of silicon/silica solution (prepared with a volume fraction 0.0005) was added to it. The resultant solution was incubated for 1 hour and then rinsed twice; finally obtaining 10 mL solution of PAH coated silicon/silica particles in DI water (volume fraction 0.001). The PAH-coated positively-charged silicon and silica particles were used in all later assembly experiments.

5.2.6 Zeta Potentials.

The particle ζ potentials were measured on a Brookhaven Instruments ZetaPALS (phase analysis light scattering) ζ potential analyzer. For the 3.3 µm amidine functionalized PSL microspheres, ζ = 48.8±1.2 mV; for the 3.01 µm silica microspheres, ζ = -55.9±1.1 mV; for the PAH coated 3.01 µm silica microspheres, ζ = 57.5±2.4 mV; for the 0.81 µm sulfate-functionalized PSL, ζ = -68.7±1.2 mV; for the 20 nm sulfate-functionalized fluorescent yellow-green PSL, ζ = -64.1±2.4 mV; for the gold particles, ζ = -50±1.3 mV; and for the silver particles, ζ = -43±1.6 mV. For the crushed silicon particles, ζ = -45.8±1.4 mV and for the PAH coated silicon particles, ζ = 60.0±0.4 mV. All the above ζ potential measurements were taken in 10 mM KCl solution at pH between 5 and 6.
5.2.7 Trimer Fabrication.

Stock solutions of each type of particle used for assembly were prepared. “Core” particles used included amidine-functionalized PSL (APSL, volume fraction 0.001), PAH-functionalized silica (SiO$_2$, volume fraction 0.001), and PAH-functionalized Silicon (Si, volume fraction 0.001). “Satellite” particles used included sulfate-functionalized PSL (SPSL, volume fraction 0.001), gold (Au, volume fraction 0.00016) and silver (Ag, volume fraction 0.0005). Specified amounts satellite particles were added to a solution of suspended core particles in a test tube, along with enough 30 mM KCl to give a final solution ionic strength of 25 mM. These test tubes were placed on a roller for 30-60 minutes, and the aggregation was quenched at the calculated time by adding 2 µL of stock 20 nm fluorescent yellow green sulfate-functionalized PSL nanoparticles (volume fraction 0.019). The solution was then diluted by adding DI water, and the resulting structures characterized by optical and electron microscopy. Table 1 gives the volume amounts and approximate quench times used to fabricate each system.

<table>
<thead>
<tr>
<th>Trimer</th>
<th>Satellite 1 added (mL)</th>
<th>Satellite 2 added (mL)</th>
<th>Core added (mL)</th>
<th>Quench Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPSL-APSL-SPSL</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
<td>30</td>
</tr>
<tr>
<td>SPSL-SiO$_2$-SPSL</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
<td>30</td>
</tr>
<tr>
<td>SPSL-Si-SPSL</td>
<td>0.05</td>
<td>-</td>
<td>0.05</td>
<td>60</td>
</tr>
<tr>
<td>Au-APSL-Ag</td>
<td>0.15</td>
<td>0.05</td>
<td>0.05</td>
<td>30</td>
</tr>
<tr>
<td>Au-SiO$_2$-Ag</td>
<td>0.15</td>
<td>0.05</td>
<td>0.05</td>
<td>30</td>
</tr>
<tr>
<td>Au-Si-Ag</td>
<td>0.2</td>
<td>0.07</td>
<td>0.05</td>
<td>60</td>
</tr>
</tbody>
</table>

5.2.8 SEM Sample Preparation.

Approximately 5 µL of the particle assembly sample (at a dilution of less than 0.0001 volume fraction) were pipetted onto a silicon wafer and left to air dry. The samples were gold
sputtered for 30 seconds to allow for better sample conductivity. Scanning Electron Microscopy (SEM) images were taken at an accelerating voltage of 5 kV and working distances between 6 and 7 mm.

5.2.9 Mechanical Stability Testing / Nanoparticle “Glue” Fusing.

The polymer nanoparticle coating of these trimer constructions can be fused by heating them in an autoclave oven, increasing the mechanical stability of the assembly. In order to study the stability of the final construction upon fusing, ultrasonication of the trimer sample, before and after fusing, was performed. Two samples of two different types of assemblies were taken. The first sample of each trimer assembly was sonicated without any fusing for 15 minutes. The second was fused by placing the solution in a test tube and heating the sample in an autoclave oven at 120 °C for 30 minutes. This fused sample was then also sonicated for 15 minutes. The degree of aggregation in each sample was then analyzed using optical microscopy. The satellites adhered to a set number of core particles in each sample were counted, giving an average “number of satellites per core” for each sample.

5.2.10 Functionality of Trimers as Catalytic Motors.

To test for catalytic activity, each trimer sample containing gold and silver satellites was observed in a 3% hydrogen peroxide solution under an optical microscope at 20× magnification. The H₂O₂ solution was first placed in a Petri dish, and 100 µL of the trimer solution (after quenching) was added. Any movement of the trimer assemblies was observed and recorded by a video camera attached to the microscope. To prepare the time lapse image (Figure 5), a frame of video was captured every 2 seconds and each frame overlaid into a single image.
5.3 Results and Discussion

5.3.1 Description of the QEA Technique

The QEA technique is a controlled aggregation technique with an important random aspect. Two or three types of particles are used in the technique: “core” particles, which are larger, and in our work have a positive surface charge; and one or two types of “satellite” particles, which are smaller and have the opposite (here, negative) surface charge of the core particles. The particles we use in this chapter are 3-5 μm in diameter for the core and 0.8-1.5 μm in diameter for the satellites. Additionally, polymer nanoparticles having a diameter of 20 nm and having the same sign surface charge as the satellites are used for quenching and fusion. A schematic of the technique can be found in Figure 5.1

With the QEA technique, the key is to control the interparticle forces temporally. Instead of destabilizing and restabilizing a stable colloidal system to induce desired aggregation, as is done in the SQF technique, the QEA technique starts with an initially unstable system, since the core particles and satellite particles have opposite charge (Fig 5.1a). The particles do not aggregate to form large clumps immediately, because the aggregation time is diffusion-limited and can be controlled by carefully adjusting the concentrations of the particles in solution. After sufficient satellite-to-core aggregation has occurred (Fig 5.1c), we then stabilize the system (Fig 5.1d-e) by functionalizing the remaining core particle surfaces with the polymer nanoparticles. The nanoparticles quickly cover the remaining core particle surfaces, preventing further satellite-to-core aggregation. The use of electrostatic attractive and repulsive forces is key, as it allows us to selectively aggregate the core particles to the satellites, and prevents satellite-satellite aggregation in solution or on the core particle surface. The specificity of the particle ordering can be contrasted with the randomness of the satellite orientations on the core. In allowing the
satellites to interact freely with the entirety of each core (and not a functionalized patch), we sacrifice the ability to orient the satellites with respect to each other.

5.3.2 Analysis of Trimers Formed Using the QEA Technique

Figure 5.2 shows scanning electron microscope (SEM) images of trimers formed from six different colloidal systems, highlighting the flexibility and non-material specificity of the QEA technique. We chose three core materials to use in trimer assembly: polystyrene latex spheres, silica spheres, and silicon shards obtained by grinding and filtering silicon powder to size. In these systems, we used positively charged core particles and negatively charged satellites. The polystyrene latex was purchased with an amidine surface functionalization, giving it a native positive surface charge in water. The silica and silicon (which had a thin native oxide passivation
layer) were natively negatively charged in water, and were functionalized with a cationic polyelectrolyte before assembly. The two negatively charged satellite systems we used were sulfate-functionalized polystyrene latex spheres, used to form two-component trimers with each core; and a binary distribution of gold and silver particles of roughly the same size and surface charge, used to form three-component trimers with each core. Because the gold and silver were synthesized and not purchased, they had a considerably larger polydispersity, but even in non-ideal systems, we were able to form three-component trimers with ease. This suggests that the QEA technique is robust: able to handle a large variety of materials, shapes, and sizes. Finally, the technique appears scalable, as the assembly happens in solution and not near any interface or in any special equipment. The importance and ease of scalability in free-solution assembly is something the authors hold in high regard.

Quenching the aggregation is a key step in the QEA process (Fig 5.1d-e). We used negatively charged, sulfate-functionalized polystyrene latex nanoparticles with an embedded fluorescent yellow-green dye to do this. Because the diffusion coefficient of a colloidal particle is inversely proportional to its radius (Stokes-Einstein) the nanoparticles have diffusion coefficients more than an order of magnitude higher than the satellites. Also, because of their size, they have a much higher number density. The nanoparticles flood the system and quickly diffuse to the bare spots on each core. We could use polyelectrolytes to halt the aggregation, although the nanoparticles have an advantage in giving the final assembly mechanical stability, which we will describe later. We did not observe any further aggregation of our systems over the course of days after assembly, and confirmed that the addition of the nanoparticles in the beginning of the experiment did not allow for any satellite-core aggregation. To confirm the presence of the nanoparticles on the cores, we examined the completed assemblies in a confocal microscope (Figure 5.3).
Figure 5.8: Colloidal Trimers Produced Using QEA Technique. a), b), and c) consist of sulfated polystyrene satellites attached to a) amidine-functionalized polystyrene cores; b) PAH-coated silica cores and c) PAH-coated silicon cores. d), e) and f) consist of gold and silver satellites attached to these same cores, respectively. The aggregation was quenched with 20 nm sulfate-functionalized polystyrene nanoparticles. Yields were typically around 15% for the two-component trimers (a, b, c) and around 8% for the three-component trimer (d, e, f). Images captured using SEM. Images are typical for each sample, which also contained bare core particles, heterodoublets, and higher-order aggregates. Scale bars are 1 μm.
5.3.3 Purification and Stability of the Assemblies

Purifying the various assemblies from the unaggregated satellites and nanoparticles can be done by sedimentation. However, further separation of the assemblies – for example, separating a core with one satellite particle from a core with two or three satellites – is more difficult. Certain trimers, for example when the core and satellites all have different material densities, may allow for the assemblies to be separated isopycnically. Additionally, field flow fractionation\textsuperscript{26},

\textbf{Figure 5.9: Confocal Fluorescence Microscopy of Quenched Trimers.} Fluorescent yellow-green nanoparticles are visible on the core of each trimer. a) Polystyrene-silica-polystyrene trimers (Fig. 2b). b) Gold-silica-silver trimer (Fig. 2e). c) Polystyrene-silicon-polystyrene trimer (Fig. 2c). All images taken with a 60x oil objective. Scale bars are 5 μm.
density gradient sedimentation\textsuperscript{27}, and hydrodynamic chromatography\textsuperscript{28} are techniques shown to provide clean separations of colloidal systems, although the throughput on these methods makes them limited. Purification of the final assemblies remains a challenge.

A final result of the QEA technique that needs discussion is the mechanical stability of fused assemblies. As discussed earlier, assembled particles that rely only on van der Waals or electrostatic attractive forces to hold them together are not generally stable and will break up under stresses such as vortexing or bath sonication.\textsuperscript{7} Fusing of polymeric components is an easy and reliable way to enhance the mechanical stability of the assemblies. As expected, we found that for trimers consisting entirely of polystyrene (Fig. 5.2a), fusing the assemblies protected them from breakup in a bath sonicator. However, even when the trimers contained only non-polymeric components, fusing the polymer nanoparticle coating was enough to hold the assemblies together. Figure 5.4 shows the results of a stability study performed on silica-core trimers (Fig. 5.2b and 5.2e). In both the two- and three-component cases, fusing the nanoparticle coating before 15 minutes of bath sonication prevented statistically significant breakup of the assemblies.

The polymer nanoparticles that cover each core particle are adhered in an ionic strength of 25 mM. The Debye screening length of the solution, which gives a measure of the expected distance between nanoparticles on the cores, is less than 2 nm. Mechanistically, it is reasonable that the nanoparticles are softening and spreading during the fusion process, adhering strongly to the core and perhaps to each other. Additionally, nanoparticles near a satellite particle may spread up onto the satellite as well. Thus, after heating, the nanoparticles are acting like glue, sticking to all parts of the assembly and to themselves, creating a strong physical bond that holds the assemblies together.
5.3.4 Three-component Motors Fabricated Using QEA

As mentioned previously, one of the primary reasons we aimed to fabricate three-component, ordered assemblies was to produce a controllable catalytic motor. To do this, we desired to add a semiconductor particle that functions as a “switch” between the gold and silver microspheres used in previous motor construction. The QEA technique has successfully been used to fabricate this assembly: a gold-silicon-silver trimer is shown in Fig. 5.2f. The gold-polystyrene-silver and gold-silica-silver trimers (Fig. 5.2d and Fig. 5.2e respectively) showed no catalytic movement at all in a 3% hydrogen peroxide solution. In contrast, due to the high native conductivity of silicon (with respect to de-ionized water), the gold-silicon-silver trimers were...
always active and moving in peroxide, as seen in Figure 5.5. This result suggests that silicon is not an effective “switch” material – it does not control the electron pathway between the metals to the extent necessary to slow the motor movement. Despite this, the QEA technique allows us to rapidly try many different core materials as semiconductor switches, resulting in the experiments found in Chapter 7.

![Autoelectrophoresis of Gold-Silicon-Silver Trimer in 3% Hydrogen Peroxide.](image)

**Figure 5.11: Autoelectrophoresis of Gold-Silicon-Silver Trimer in 3% Hydrogen Peroxide.** Optical microscopy image taken at 20x magnification. Time-lapse image, overlays are 2 seconds apart. Scale bar is 10 μm.

### 5.3.5 Optimization of Trimer Yield: Diffusion-Limited Aggregation of Core/Satellite Assemblies

In order to optimize the yield of the desired trimers – and to avoid undesirable side-products – we modeled the QEA process as a diffusion-limited aggregation. The modeling of our assembly technique as a diffusion-limited aggregation process, with the equation found mentioned earlier, follows. We make a few simplifying assumptions at the outset. Because the ionic strength of our systems is 25 mM, we can assume that electrostatic interactions are short-
range only, and we neglect interparticle force interactions, as well as hydrodynamic interactions. Since the core particles have a large surface area, we approximate that the available area on which satellites can dock remains unchanged with time. Additionally, we examine small times, when only 1 or at most a few satellites have aggregated onto the core; therefore, we approximate that the diffusion coefficient of the core + satellite assemblies is approximately equal to the diffusion coefficient of the core alone. Although core particles repel each other electrostatically, it is possible that a satellite could bridge two core particles. We assume that the core concentration is kept low, so that this occurrence is unlikely; therefore, we mathematically model the core concentration as constant in time.

We begin with the diffusion equations, following Hiemenz. The diffusive flux \( J \) of particles of type 1 (satellites) with diffusion coefficient \( D_1 \) and number per unit volume \( n_1 \) arriving at a distance \( r \) from a reference particle of type 2 (cores) is given by

\[
J_1(r) = -D_1 \frac{dn_1}{dr}
\]

Since we assume that the core particles do not “fill up”, we model a steady flux of satellite particles diffusing toward the cores, so that \( J_1 \) is constant and uniform. This equation is integrated with the boundary conditions \( n_1(r \to \infty) \to n_{b1} \) and \( n_1(r = a_1 + a_2) = 0 \), where \( a_1 \) and \( a_2 \) are the respective particle radii and \( n_{b1} \) and \( n_{b2} \) are the respective bulk particle number densities. To account for the diffusive flux of the reference particle, \( D_1 \) is replaced by \( D_{12} = D_1 + D_2 \).

It follows that the rate of “consumption” of particle 1 as it aggregates onto particle 2 is

\[
\frac{dn_{b1}}{dt} = -4\pi(a_1 + a_2)(D_1 + D_2)n_{b1}n_{b2}.
\]

Combining this with the Stokes-Einstein relation \( D = kT / 6\pi\eta a \) gives

\[
\frac{dn_{b1}}{dt} = -(2kT(a_1 + a_2)^2 / 3\eta a_1 a_2)n_{b1}n_{b2}
\]

where \( kT \) is the thermal energy and \( \eta \) is the solution viscosity. If, as mentioned earlier, we take the bulk concentration of core particles to be constant, and integrate this rate to obtain a time-dependent concentration of satellites, we obtain the number of satellites in the bulk as a function of time:
\[ n_{b1}(t) = n_{b1}^i \exp\left\{ -\frac{2kTn_{b2}(a_1 + a_2)^2}{3\eta a_2} \frac{t}{n_{b1}^i} \right\} \quad \text{Eq. 5.4} \]

where \( n_{b1}^i \) is the initial satellite number density.

We now know how the satellites aggregate to the cores as a function of time, so we must next consider when it is optimal to quench the aggregation. The expected time-dependent distribution of satellites on the cores can be described by a Poisson distribution\(^{30}\), as we have assumed that the aggregated satellites are equally likely to be found on any given core. The Poisson distribution with mean \( \mu \) is given as:

\[ f(x) = \frac{\mu^x}{x!} e^{-\mu} \quad \text{Eq. 5.5} \]

Applied to our system, this probability distribution allows us to calculate the expected fraction of cores with \( x \) satellites depending on the average number of satellites per core, \( \mu \). It is trivial to show that the maximum value of \( f(x) \) for a certain value of \( x \) occurs when \( x = \mu \). In other words, to maximize the number of trimers (\( x = 2 \)), we would quench the aggregation after two satellites have aggregated for each core particle. Likewise, to maximize cores with four satellites, we would quench when the number of aggregated satellites is four times the number of cores.

For two-component trimers, we want the number of aggregated satellites to be twice the number of cores: \( n_{b1}^i - n_{b1}(t) = 2n_{b2} \). Substituting into \textit{Eq. 5.5} and solving for \( t \) gives a characteristic quench time of

\[ \tau = \frac{3\eta a_2 \ln \left( \frac{n_{b1}^i}{n_{b1}^i - 2n_{b2}} \right)}{2kTn_{b2}(a_1 + a_2)^2} \quad \text{Eq. 5.6} \]
For three-component trimers, we assume that each type of satellite is aggregating to the cores independently. Therefore, we want to maximize the number of cores containing one of each satellite \( (x = 1) \) and therefore should quench when \( n_{bi}^i - n_{bi}(t) = n_{b2} \). This gives a characteristic quench time to obtain the highest fraction of 3-component trimers:

\[
\tau = \frac{3\eta a_1 a_2 \ln \left( \frac{n_{bi}^i}{n_{b1}^i - n_{b2}} \right)}{2kTn_{b2} (a_1 + a_2)^2}
\]

Eq. 5.7

There is no theoretical reason that the satellites and core must be different sizes. However, when the diffusion coefficient of the cores becomes comparable to that of the satellites, we run an increased risk of seeing core-satellite-core aggregates. This occurs when the timescale for core aggregation (which can be estimated in a similar manner) is on the order of the calculated quench times for the system. This can be overcome by keeping the core concentration low and the relative concentrations of each satellite high.

The QEA technique can also be taken to assemble larger numbers of satellite particles to each core. Unfortunately, the distribution grows broader as the aggregation is allowed to progress further. Figure 5.6 displays the expected particle distribution for three-component trimers, as well as some higher order aggregates.
Figure 5.12: Theoretical Distributions For Three-Component Systems. Each distribution maximizes a particular configuration, and shows the expected fraction of core particles with the number of each of two satellites. a) One of each satellite per core (three-component trimers), theoretical maximum yield 13.5%. b) Two of the first satellite, one of the second, theoretical maximum yield 10.0%. c) Two of each satellite particle, theoretical maximum yield 7.3%. d) Two of the first satellite, three of the second, theoretical maximum yield 6.1%.

5.4 Conclusion

The Quenched Electrostatic Assembly technique has been used to create multicomponent, ordered assemblies out of several types of particles and materials. While colloidal trimers are the focus of the technique in this work, QEA can also be used to form colloidal heterodoublets, as well as even higher-order aggregates, all depending on the quench
time and initial fractions of core and satellite particles. The technique is not material specific, is scalable, and forms assemblies that are both colloidally and mechanically stable.

Several types of trimer assemblies containing functional materials have been built. These include gold-polystyrene-silver (Fig 5.2d) and gold-silica-silver trimers (Figs 5.2e), neither of which showed any activity as a colloidal motor. This lack of activity was expected, since both the polystyrene and silica cores are far too insulating to allow for any electron transport between the metals. We have also created gold-silicon-silver trimer assemblies, which do undergo auto-electrophoresis (Fig 5.5). Because the un-doped silicon has a high native conductivity relative to the surrounding solution, it is not effective as an on/off switch. Therefore, a current aim is to prototype a semiconductor particle that can be switched on/off by an external light source. Armed with the QEA technique, this is further explored in Chapter 7.

5.5 Acknowledgements &Permissions

Chapter 5 is a modified version of the author’s publication:


http://pubs.rsc.org/en/content/articlelanding/2010/cp/c0cp00254b

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Fluoview 1000 confocal laser scanning microscope, and Erin Golden for her contribution to the initial stages of the research.

5.6 References


Chapter 6

Dissolution-Induced Fluid Pumping in Disturbed Geologic Formations

6.1 Introduction & Background

In closed geologic formations, thermodynamic equilibrium has been established between the rock and the surrounding water over millions of years. However, when the formation is disturbed, further dissolution of the minerals will occur. This physical phenomenon results in the formation of local ion gradients that originate at the rock surface. The gradients can in turn drive microflows and particle movement along the mineral surfaces and in pores by the mechanism of diffusiophoresis. Diffusiophoresis is a well-understood flow mechanism; however, experimentally, this mechanism has been studied primarily using imposed salt gradients. Here, we describe how, through the dissolution and passivation of geologic materials, self-generated ionic gradients can produce phoretic microflows that are quite efficient, even in micro and nanochannels that are ubiquitous in rocks. Because of the extensive occurrence of calcium carbonate in geologic formations, it was used as the model system. Other materials (barium carbonate, dolomite, and calcium sulfate) show similar behavior. Unlike pressure-driven convective fluid flow, diffusiophoretic flows can easily penetrate micro/nanoscale pores, and the flows persist as long as the gradient of ionic strength persists. Our research therefore has major implications for both natural and artificial processes that result in disturbed geologic systems, such as earthquakes, mining, building construction, and oil and gas extraction involving fracturing of the rock and/or injection of water. The introduction of air, water, acid mine drainage, or fracking fluids can amplify the effects of the flows.
As a simple test case, we used calcium carbonate (CaCO$_3$) microparticles to drive localized microflows both in open fluid and close channels. CaCO$_3$ can be produced using a simple aqueous precipitation synthesis of Na$_2$CO$_3$ with CaCl$_2$.$^5$ Saturated solutions of roughly spherical calcium carbonate particles (initial radii $a = 1.5$ to $3$ μm) were diluted with DI water. Individual CaCO$_3$ particles were settled onto bare glass substrates. Sulfated polystyrene latex (sPSL) particles with $a = 0.7$-1.5 μm were added as tracers to observe the resulting flows.

6.2 Experimental Methods & Materials

6.2.1 Materials

For calcium and barium carbonate microparticle synthesis, sodium carbonate Na$_2$CO$_3$, calcium chloride CaCl$_2$, and barium chloride BaCl$_2$ were obtained from Sigma-Aldrich Chemicals, USA. Solutions of 0.33 M Na$_2$CO$_3$, CaCl$_2$, and BaCl$_2$ were prepared. Two sizes of sulfate-functionalized polystyrene latex microparticles ($d = 1.4$ μm ± 2.1%, and $d = 3.0$ ± 2.4%, both had w/v = 4.0%) were purchased from Interfacial Dynamics Corporation, Portland, OR. For particle surface functionalization, sodium polystyrene sulfonate (MW ~70,000) was obtained from Sigma. Calcite and dolomite shale samples (~1 mm square) were obtained from Petrobras (Rio de Janeiro, Brazil). Local gypsum crystal (10x2x2 cm, broken into 50 μm shards) was obtained from Creekside Rocks and Gems, Bellefonte, PA. Deionized (DI) water used in all aqueous solutions came from a Millipore Corporation MilliQ system, with specific resistance greater than 1 MΩ·cm (due to equilibration with CO$_2$ in air).
6.2.2 Calcium and Barium Carbonate Microparticle Synthesis

A simple precipitation synthesis was used to synthesize the calcium and barium carbonate microparticles. In both cases, 25 mL of a 0.33 M solution of CaCl$_2$ or BaCl$_2$ was stirred at high velocity on a magnetic stirrer. An additional 25 mL of 0.33 M Na$_2$CO$_3$ was then rapidly added to the solution, which turned a milky white as the carbonate particles precipitated. The solution was stirred for an additional 1 – 2 min., and then quenched with 50 mL of DI water. To remove the remaining Na$^+$ and Cl$^-$ ions, the particle solutions were rinsed by repeated centrifugation and resuspension in DI water using a Sorvall Biofuge Primo Centrifuge from Kendro Laboratory Products. The rinsing procedure was typically repeated 2-4 times, with additional rinsing steps significantly affecting the microparticle size through carbonate dissolution. The CaCO$_3$ particles were found to be roughly spherical, with a polydispersity of ~50% and average radius ~3.5 μm. The BaCO$_3$ particles were found to be smaller (a ~.75 μm, polydispersity ~50%), and more shard-like.

6.2.3 Observation of Pumping Behavior of Carbonate Microparticles

To observe the pumping behavior, the carbonate microparticles particles were imaged using a Nikon Eclipce TE2000-U inverted optical microscope, typically at 40x magnification. First, the concentrated carbonate particle solution was diluted to the desired concentration using DI water and 500 μL was quickly pipetted into a glass-bottomed petri dish. An additional 500 μL 0.1% w/v solution of tracer sPSL particles was then added to the dish and the solutions mixed and observed.
6.2.4 Observation of Pumping Behavior of Natural Rock Samples

Similar to the procedure in section 6.2.3, calcite, dolomite, and gypsum rock samples were placed in DI water in a glass bottomed petri dish. Then, 0.1% w/v tracer particle solutions were added and the resulting movement observed using optical microscopy. In certain cases, the experiments were performed in open capillaries that contained the tracer particle solution, to simulate the effect of dissolution into a microchannel or pore.

6.2.5 Fabrication and Characterization of Calcium Carbonate Heterodoublet Micromotors

Calcium carbonate microparticles have nearly no zeta potential in DI water solutions. As a result, they easily aggregate with themselves and with polystyrene microspheres. The QEA technique described in Chapter 5 was used to form CaCO$_3$-sPSL heterodoublet micromotors. A solution was prepared with CaCO$_3$ microparticles (volume fraction $\phi = 0.001$), 3.0 μm diameter sPSL particles ($\phi = 0.001$), and in the presence of saturated calcium carbonate salt (~0.1 mM) was allowed to aggregate for 15 min. Then, a solution of 20 μM sodium polystyrene sulfonate was added to the particles, quenching the aggregation by adsorbing to and giving the calcium carbonate particles a negative surface charge. The solution of stable aggregates, which included sPSL-CaCO$_3$ heterodoublets was rinsed, resuspended in DI water, and observed using optical microscopy on bare glass substrates.
6.3 Results and Discussion

6.3.1 Analysis of Calcium Carbonate Micropumps

In this case of a solitary calcium carbonate “micropump” settled onto glass in DI water and surrounded by sPSL tracer particles, the particle flowfield is readily described. Tracer particles are pulled in from above the plate to the micropump surface. They collect at and move down the surface of the micropump, until, upon reaching the substrate, they are ejected radially outward into solution. Figure 6.1a shows both a time lapse optical image and a vector field plot of the tracers being pumped along the glass substrate. Movement away from the micropump is rapid, and then decays with distance until Brownian motion dominates the particle movement 10s of μm away. Interestingly, tracers that approach the pump at shallow angles are ejected without ever reaching the pump surface.

The observed flows are neither pressure-driven nor density-driven. We know this because as discussed later, the direction of the tracer movement depends on the surface properties of the particle and can be reversed by altering particle zeta potentials. Additionally, in high ionic strengths (> 50 mM), the flows disappear. Rather, the microflows that we observed are diffusiophoretic flows resulting from the dissolution of CaCO₃, which is ubiquitous in shales and other formations. Phoretic movements like electrophoresis and diffusiophoresis – and similarly, electroosmosis and diffusioosmosis – are known to be highly efficient even in micro and nanoscale pores and channels. This is in stark contrast to pressure-driven flows, which by the Hagen-Poiseuille equation become vanishingly small in micro or nanoscale channels. The streamlines in bulk solution resulting from the electrophoretic movement of a sphere are somewhat complex but known. The electroosmotic flow around a lone sphere attached to a flat, charged plate is also known. By combining the electroosmotic flow of the fluid with the
electrophoretic velocity of charged colloidal particles, we can ‘pump’ those particles and the surrounding fluid in complex ways, simply through the dissolution of calcium carbonate (see Figure 6.2).

How are the diffusiophoretic flows generated? In large number densities, CaCO$_3$ particles can be considered stable against dissolution since they readily saturate water. CaCO$_3$ is sparingly soluble in deionized water, with a solubility product constant of 3.36×10$^{-9}$ M$^2$ at 20° C.$^8$ However, when a concentrated suspension of CaCO$_3$ microparticles is diluted with fresh or unsaturated water, dissolution begins to occur at the particle surface into the fluid (see Sec 6.3.2 and 6.3.3). The primary ions resulting from this dissolution are Ca$^{2+}$, HCO$_3^-$, and OH$^-$. At low volume fractions of particles, the calcium carbonate can be treated as dissolving into an infinite bath. Although eventually the particles disappear from the system, during the dissolution process there is a radial concentration gradient of ions surrounding the particle.

The three ions resulting from each molecule of dissolved calcium carbonate have very different hydration radii, and therefore, quite different diffusion coefficients$^8$: At 20 C the OH-ion has a diffusion coefficient of $D = 5.27 \times 10^{-9}$ m$^2$/s, while $D_{\text{HCO}_3^-} = 1.19 \times 10^{-9}$ m$^2$/s and $D_{\text{Ca}^{2+}} = 0.792 \times 10^{-9}$ m$^2$/s. Because of these differences, the concentration of OH$^-$ ions at a given distance from the microparticle would be slightly higher than the concentrations of the other two ions, except that Columbic forces spontaneously give rise to an electric field in order to maintain electroneutrality. Because particles or surfaces in aqueous media become charged, for example due to dissociated charge groups or metal ion substitution, an oppositely-charged electrical double layer (EDL) forms in a thin layer around particles. The electric field resulting from maintaining electroneutrality acts on the charged fluid in the EDL, generating a flow at the surface. This overall process of an ion gradient effecting an electric field which drives electrokinetic flows is called diffusiophoresis.$^3$
Figure 6.1 Time-lapse (a,d), vector field (b, e) and radial speed plots (c, f) for one single pump and two interacting pumps, respectively. These systems contain only calcium carbonate pumps and 1.4 μm sulfate-functionalized polystyrene latex tracer particles (sPSL) in DI water, and are filmed on a bare glass substrate using an inverted microscope. Optical microscopy time-lapse images were taken at 40x magnification with overlays every 0.2 s. Scale bars in these images are 10 μm. In the vector field plots, axes are distance in μm. The black circles represent the location of the micropumps, and the vector arrows represent the tracer particle direction and speed in μm/s at the substrate surface. The plots were generated by tracking the movement of 750-1000 particles over 0.3 seconds. In (c), the radial speeds of all sPSL tracers sampled in (b) are plotted against the distance of those tracers from the center of the lone calcium carbonate micropump. In (f), the radial speed of tracer particles within 6 microns of the line between the two micropumps in (e) (boxed area shown) is plotted against the distance of those tracers from the midpoint between the two pumps. In both cases, curves have been added to guide the eye.
In the case when two pumps are near enough that their flowfields interact, a stagnation point exists at the midpoint between the pumps. Tracers ejected from one particle toward the other move slowly and often come to a stop before escaping in a direction orthogonal to their initial movement. Figure 6.1c shows two pumps interacting in such a manner. Additionally, the pump on the lower left demonstrates another unusual phenomenon. In this case, two large tracer particles (anomalous to the purchased sPSL suspension) have attached themselves to the pump surface, likely due to van der Waals forces. Once there, these large tracers began to ‘direct the flow’ of the other tracers like a type of micro-nozzle. The presence of additional fixed, charged surfaces generates additional local electroosmotic flow in the solution. As a result, the smaller, mobile tracers favor movement along these surfaces. Further experiments confirm the nozzling phenomenon: by adding additional fixed charged surfaces, the flow of tracers can be focused or directed in the solution around our pumps. This opens the possibility for designing complex flow patterns in dissolving mineral systems as well as mechanisms for microparticle motility, as observed later in this chapter.

Figure 6.2 Contributing diffusiophoretic effects in the micropump system. The calcium carbonate particle dissociates into three ions in DI water. Due to difference in diffusion coefficients of these ions, an electric field arises in the same vector direction as the radial concentration gradient in order to maintain electroneutrality. The electric field generates an electroosmotic flow along the charged substrate (in this work, bare glass in water). Charged tracer particles in the solution have an electrophoretic velocity either up or down the gradient, depending on the sign of their charge. The overall flow profile of the tracers is the superposition of their electrophoretic flow and the electroosmotic flow of the surrounding solution.
6.3.2 Aqueous Equilibrium of Calcium Carbonate

For diffusiophoresis of a particle in an ionic gradient to occur, the ions must have significantly different aqueous diffusion coefficients. This section aims to identify the most prevalent species, so that the relative diffusion coefficients can be compared. Therefore, identification of the ions present in the system is tremendously important for accurately analyzing diffusiophoretic and osmotic flows resulting from dissolution of mineral systems. The equilibrium of calcium carbonate with water is complex, with the total solubility of calcium carbonate depending on both the partial pressure of atmospheric carbon dioxide and the system pH.

The four primary equilibrium reactions that affect calcium carbonate dissolution are as follows:

\[
\begin{align*}
\text{Equilibrium reaction} & \quad K_{eq}, \; 298 \text{ K} \\
\text{CaCO}_3(s) & \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} & 3.36 \times 10^9 \\
\text{CO}_3^{2-} + \text{H}^+ & \leftrightarrow \text{HCO}_3^- & 2.14 \times 10^{10} \\
\text{HCO}_3^- + \text{H}^+ & \leftrightarrow \text{H}_2\text{CO}_3(aq) & 2.24 \times 10^6 \\
\text{H}_2\text{CO}_3(aq) & \leftrightarrow \text{H}_2\text{O} + \text{CO}_2(aq) & 5.88 \times 10^2
\end{align*}
\]

Along with the water autoionization:

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \quad 1.01 \times 10^{-14} \]

the charge neutrality condition:

\[ 2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \]
and with the Henry’s Law, which determines the concentration of dissolved CO$_2$ from the partial pressure of atmospheric CO$_2$:

$$[CO_2^{(aq)}] = k_H^{CO2} p_{CO2}$$

Where $k_H^{CO2}$ is the temperature-dependent Henry’s Law constant for CO$_2$ in water (for our system at 25 deg C, $k_H^{CO2} = 3.4 \times 10^{-2}$ M/atm). In fact, many of our normally-simple equations used for equilibrium would be modified at the enormous pressures, temperatures, and ionic strengths prevalent in geologic formations; further thermodynamic experiments and modeling might be required to understand the activity coefficients and other modeling features. Because any CO$_2$ evolution from small amounts of dissolving calcium carbonate is not expected to increase the local CO$_2$ pressure (0.0314 atm), Henry’s Law serves as a starting point for determining the overall solubility of CaCO$_3$ in our systems as it fixes the concentration of dissolved CO$_2$ at $1.07 \times 10^{-5}$ M. Now, the degrees of freedom in the system is 0, (5 equilibrium equations + 1 charge neutrality condition – 6 concentrations: Ca$^{2+}$, CO$_3^{2-}$, HCO$_3^-$, H$_2$CO$_3$, H$^+$, OH$^-$), and the final concentrations of each species can be determined for when the system reaches saturation:

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>$1.11 \times 10^{-4}$</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>$3.01 \times 10^{-5}$</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>$7.24 \times 10^{-5}$</td>
</tr>
<tr>
<td>H$_2$CO$_3$</td>
<td>$1.82 \times 10^{-8}$</td>
</tr>
<tr>
<td>H$^+$</td>
<td>$1.12 \times 10^{-10}$</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>$9.00 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

At concentrations lower than saturation, the ratio of bicarbonate to carbonate ion is calculated to
be even higher. Thus, the three primary ions present in the system during dissolution are Ca$^{2+}$, HCO$_3^-$, and OH$^-$. 

6.3.3 Concentration Profile and Diffusiophoretic Velocity Profile for a Calcium Carbonate Sphere Dissolving into an Infinite Bath

Concentration Profile:

To fully understand and analyze the velocity profile of fluid and tracer particles moved through diffusioosmotic and diffusiophoretic pumping of a dissolving mineral microsphere, we must first understand the concentration gradient of the ions in the system. An appropriate model of the calcium carbonate microsphere system is that of a sphere dissolving into an infinite bath.

We make the assumptions that the microsphere has radius $a$ with a non-moving solid-liquid interface, that there is a constant surface ionic concentration $C_s$ equal to the saturation concentration of calcium carbonate at $r = a$, the overall diffusion coefficient of the ions is a constant, $D$, and that the sphere is dissolving into an infinite bath with concentration $C_b$.

Fick’s Second Law describes this situation (unsteady-state diffusion):

$$\frac{\partial C}{\partial t} = D \nabla C$$

with boundary conditions:

$$C(r = a, t) = C_s$$
$$C(r = \infty, t) = C_b$$

And initial condition:

$$C(r, t = 0) = C_b$$
The solution for this concentration profile is:

\[ C(r, t) = \left( C_s - C_b \right) \frac{a}{r} \text{erfc} \left[ \frac{r-a}{\sqrt{4Dt}} \right] + C_b \]  

Eq.6.1.

As time progresses, the error function complement goes to 1 and we reach the expected steady-state concentration profile:

\[ C(r) = \left( C_s - C_b \right) \frac{a}{r} + C_b \]  

Eq.6.2.

**Time to Steady State:**

It is convenient to use the steady-state concentration profile for analyzing our diffusiophoretic velocities, but to do so we must be sure that we have observed the system after it has reached steady state. We typically observe tracer movement up to 80 μm away from the micropump. In this case, for our system with \( r = 3.0 \times 10^{-6} \) m, \( D = 1.70 \times 10^{-9} \) (weighted harmonic average of the three primary ions), \( C_s = 1.11 \times 10^{-4} \) (as determined above) and \( C_b = 0 \), we should reach 95% of the steady state concentration value at a distance of 80 μm in a time of \( t = 111 \) s. Since our experiments are typically performed over the course of 10-20 minutes, with a 5 minute preparation time, we expect that the observed area of our system should be at roughly steady state throughout the course of experimentation.

**Effects of Multiple Pumps in the System:**

While the resulting concentration profile due to the presence of multiple pumps in the system can be explicitly calculated (e.g., using a finite element method), the term \( C_b \) in our
equations instead allows us to assign a bath concentration profile as a ‘background’ value, which would increase directly with the number of calcium carbonate particles present in the sample.

**Diffusiophoretic Velocity of a Tracer Particle:**

The equation for diffusiophoresis of a tracer particle in a concentration profile near a charged surface is given as:

\[
U(r) = \frac{\nabla C(r)}{C(r)} \left( \frac{D_c - D_a}{D_c + D_a} \right) \left( \frac{k_b T}{\eta} \right) e (\zeta_p - \zeta_w) + \ldots
\]

\[
\ldots \frac{\nabla C(r)}{C(r)} \left( \frac{2e}{\eta} \right) \left( \frac{k_b T}{e} \right)^2 \ln \left[ 1 - \tanh \left( \frac{e \zeta_w}{4k_b T} \right) \right] - \ln \left[ 1 - \tanh \left( \frac{e \zeta_p}{4k_b T} \right) \right]
\]

Eq. 6.3.

where \( D_c \) and \( D_a \) are the diffusion coefficients of the cation and anion, respectively, \( \zeta_p \) and \( \zeta_w \) are the zeta potentials of the particle and wall, respectively, \( k_b T \) is the thermal energy, \( e \) is the electron charge, \( \varepsilon \) is the permittivity of the medium, and \( \eta \) is the viscosity of the medium.

For our steady-state concentration profile, \( \frac{a(C_b - C_s)}{(C_b + \frac{a(C_s - C_b)}{r}) r^2} \)

\[
\frac{\nabla C(r)}{C(r)} = \frac{a}{r^2} \left( \frac{C_b - C_s}{C_b + \frac{a(C_s - C_b)}{r}} \right)
\]

with the special case of no bath concentration:

\[
\frac{\nabla C(r)}{C(r)} = \frac{1}{r}
\]

One interesting observation that can be made from these equations is that the surface concentration has little effect on the overall velocity, especially when it is much higher than the bath concentration.
Although it is well-understood how to predict the direction of movement for the tracer particles using the concepts of diffusiophoresis and diffusiophoresis, the actual prediction is not always trivial. As shown in Figure 6.2, the electroosmotic flow along a negatively-charged substrate is in the opposite direction from the electrophoretic movement of a negatively charged tracer particle. To predict the direction of particle movement in this system, it is not enough to use only the particle zeta potentials (in millivolts); we must use the difference in zeta potentials of the tracer and wall ($\zeta_p - \zeta_w$)\textsuperscript{10}. When $\zeta_p - \zeta_w < 0$, the tracer will move inward. When $\zeta_p - \zeta_w > 0$, the tracer is driven outward, as seen in our micropump system. However, an additional complexity is that the zeta potentials in our system are not uniform with radial position nor with time. The ionic concentration surrounding the pump changes significantly with radial distance, and changing the ionic strength changes the zeta potential for a given surface charge. The effect of large, multivalent ions like Ca\textsuperscript{2+} on the surface charge groups of colloidal particles is especially important. These have been previously studied, although primarily in the presence of a fully-dissociated salt (such as CaCl\textsubscript{2})\textsuperscript{11}. In our system, the saturation concentration of CaCO\textsubscript{3} is less than 1 mM, but the ions still have a large effect on the zeta potentials of the particle and the wall. The table shows our measured zeta potentials of sPSL and bare silica particles in the presence of saturated calcium carbonate solution with and without 10 mM potassium chloride salt.

As a result, the speed of the tracers depends on both the concentrations of salts and the gradients of concentrations in the usual way for diffusiophoresis, but they also depend upon the concentration because the zeta potentials vary over short distances. An example of how complex determining the direction of particle movement can be resulted from the zeta potential study for the sPSL particle zeta potential. Normally the sPSL zeta potential is suppressed in the presence of CaCO\textsubscript{3} solution, but it can be restored by the addition of KCl ions. When the micropump experiments were repeated with a 10 mM KCl solution, the direction of the tracer movement reversed as expected. At higher KCl concentrations (>100 mM), the motions ceases due to ionic
screening, which causes the diffusiophoretic and diffusioosmotic flow mechanisms to become negligible.

From modeling, we would expect the velocity to be roughly inverse to the radial distance. However, this does not take into account the changing zeta potentials of both the particle and the wall as a function of calcium carbonate ion concentration. Our observed velocity profiles therefore have a more exponential decay shape. A proper zeta potential vs. concentration correlation is needed for a more comprehensive velocity profile.

We can, however compare the observed velocities of tracers near to the pump surface with the velocities expected given the measured zeta potentials in the system:

**Table 6-1: Effect of KCl ions on zeta potentials and micropump flow**

<table>
<thead>
<tr>
<th>Condition</th>
<th>$\zeta_p$ (mV)</th>
<th>$\zeta_w$ (mV)</th>
<th>Predicted Speed (μm/s)</th>
<th>Observed Speed (μm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$ no other salt</td>
<td>-27</td>
<td>-43</td>
<td>39.0</td>
<td>35.9</td>
</tr>
<tr>
<td>CaCO$_3$ 10 mM KCl</td>
<td>-71</td>
<td>-65</td>
<td>-19.0</td>
<td>-1.03</td>
</tr>
</tbody>
</table>

Calculations were made, predicting the speed at a radius of 6 μm from the center point of the pump, with a pump radius of 3 μm, a water viscosity of .001 Pa s and permittivity of 78 $\varepsilon_0$, and a thermal energy of $4 \times 10^{21}$ J. Observed speeds were estimated using frame-by-frame particle tracking, similar to the analysis in Figure 6.1.

One consideration in using these CaCO$_3$ micropumps to model ion-driven flows in geological systems is that the portfolio of concentration gradients generated in real systems are
much more complex than around our pumps. The velocity field between two pumps in close proximity can be approximated by the addition of the individual velocity fields around each pump (see Figure 6.1d). When many pumps interact, the overall speed of the tracer particles decreases, but the motion can be seen over even millimeter-scale distances, likely due to the increasingly complex ion gradient profile. Figure 6.3 shows these results, studied by varying the surface fraction of pumps on the glass substrate.

Figure 6.3 Effect of surface concentration of calcium carbonate micropumps on tracer particle speed (circle) and length of transport decay (x). By fitting exponential decay functions to tracer velocity data sampled from optical microscope videos of the micropumps, the speed of the tracers at the surface of each pump (the theoretical maximum) and the radial distance at which the tracer speed decays to its half-maximum can be determined. As the surface fraction of calcium carbonate micropumps in a given sample increases, the speed of the tracer particles sharply decreases, while the length over which the speed decays grows larger. These systems were similar to the systems examined in Figures 6.2, containing only micropumps and sPSL tracers in DI water on bare glass substrates.
6.3.4 Flows Generated by Other Geologic Systems

Calcium carbonate microparticles have served as a model system to study diffusiophoretic microflows, but they are not the only mineral that drives flow. Indeed, we have found that the dissolution of several different minerals drive diffusiophoretic flows, as shown in Figure 6.4. Barium carbonate microparticles (Fig. 6.4a) synthesized in a similar manner to the CaCO$_3$ particles show nearly identical behavior. In fact, the pumping of the tracers is even faster for comparable particle surface fractions, due to the greater disparity in ionic diffusion coefficients between the Ba$^{+2}$ and OH$^-$. Dissolution of naturally occurring gypsum (hydrated calcium sulfate) crystals (Fig 6.4b) also drives tracer particle motion. Interestingly, although calcium sulfate is much more soluble than calcium carbonate ($K_{sp} = 3.41 \times 10^{-5}$), the tracers move more slowly due to a smaller difference in the ion diffusion coefficients of Ca$^{2+}$ ($D = 0.792 \times 10^{-9}$) and SO$_4^{2-}$ ($D = 1.07 \times 10^{-9}$).\textsuperscript{8} It is not the magnitude of the solubility of the ions that determines the speed of the flow, but the difference in diffusion coefficients of the ions, in keeping with the diffusioosmotic mechanism. Finally, both naturally-occurring calcite and dolomite, both obtained from an oil reservoir, behaves identically to the calcium carbonate micropumps, except for acting on a much large length scale (Fig 6.4c) due its larger size.
One interesting observation made during the experiments with geologic calcite rock was that, on occasion, microparticles would break off the rock during experimentation (likely due to short-lived hydrodynamic flows during addition of tracer particles), coat themselves in tracer particles, and move independent of the overall diffusioosmotic flow. Diffusiophoretic heterodoublet motors have been previously studied in the Velegol lab\textsuperscript{12}, and this movement

**Figure 6.4: Time-lapse optical microscopy images of diffusiophoretic pumping of sPSL tracer particles in mineral systems.** a) Barium carbonate microparticle pumping 1.4 μm sPSL tracer particles outward, overlays are 0.33 sec apart, scale bar is 20 μm. b) Gypsum (calcium sulfate) crystal attracting 3.0 μm sPSL particles inward, overlays are 2 sec apart, scale bar is 50 μm. d) Large natural calcite rock slice pumping 3.0 μm sPSL tracers outward in a 0.9 mm square glass capillary, individual captures are 66.7 seconds apart, scale bar is 200 μm

**6.3.5 Calcium Carbonate – sPSL Heterodoublet Motors**
seemed analogous. To study this phenomenon more closely, we used the QEA technique outlined in Chapter 5 to construct CaCO$_3$-sPSL heterdoublets and aggregates. The CaCO$_3$ particles were kept stable and prevented from sticking to the glass substrate by functionalization with an anionic polyelectrolyte, polystyrene sulfonate.

Figure 6.5 shows a time-lapse image of a CaCO$_3$-sPSL (3 μm diameter) heterdoublet moving freely in a directed fashion over a glass substrate – a diffusiophoretic dissolution-powered micromotor. This exciting result suggests that calcium carbonate particles can act as a motor ‘batteries’ – storing energy that can be used to drive motion of charged colloidal assemblies through dissolution and subsequent diffusiophoretic flow.

![Figure 6.5: Time-lapse optical microscopy of a diffusiophoretic sPSL-CaCO$_3$ heterodoublet micromotor.](image)

In conclusion, using calcium carbonate as a model, we have shown that ion dissolution from a mineral can drive microscale flows and particle movement in the surrounding aqueous medium. Diffusiophoretic pumping is particularly efficient for movement through micro and
Other flow mechanisms such do not work well in these narrow channels; for example, the Hagen–Poiseuille fluid speed for a pressure-driven flow in a channel depends upon the radius squared, and typical numbers indicate speeds less than 1 nm/s. Water injection and rock fracturing are commonly practiced in oil wells and now in gas shales, and ion gradients will occur as a result. While the overall flows involve millions of gallons of water, the mechanism of obtaining the desired petroleum or gas out of dense rocks might depend significantly on mineral-driven microflows. Furthermore, in geologic events like earthquakes, microflows might bleed chemical species from micro or nanochannels in rock to larger-scale bulk flows.

6.5 Acknowledgements & Permissions

Chapter 6 is a modified version of the author’s publication:


Dissolution-Induced Fluid Pumping in Disturbed Geologic Formations, submitted to Science.

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6.6 References


Chapter 7

Photoresponsive Metal - Cadmium Sulfide Colloidal Micromotor Assemblies

7.1 Introduction & Background

Autonomous colloidal micromotors are growing increasingly complex. These motor particles respond to the presence of electrochemical species in their local environment by creating localized electric fields\(^1\), ionic concentration gradients\(^2\), or even pressure differences (through bubble nucleation)\(^3\) that drive both autonomous motion of each motor and of the surrounding fluid. Recently, motor mechanisms have been developed that respond to ultraviolet light, i.e., in addition to\(^4\) or instead of\(^5\) converting electrochemical energy to mechanical motion, they utilize light to perform chemical reactions to drive localized gradient formation. By using light, control of the speed and collective behavior of the motor particles can be exercised. In this work, micron-sized particles of the semiconductor cadmium sulfide are added to both existing motor systems and are used to develop new motor mechanism. Because CdS has a band gap of 2.4 eV\(^7\) (corresponding to blue-green light), it responds to light in the visible spectrum, and therefore allows the motor assemblies to be manipulated using a mercury arc lamp used for simple fluorescence microscopy experiments.

Bimetallic colloidal rods, synthesized using a templated electrodeposition technique, were among the first colloidal motor systems.\(^1\) When placed in solutions of water - hydrogen peroxide, these nanorods of platinum-gold or gold-silver catalytically decompose the peroxide, with each half reaction occurring selectively on each metallic end. The flow of electrons through the rod (from one metal to the other) is accompanied by a flow of protons through the
surrounding solution, creating an electric field. If the rods have a surface charge, they move through the process of autoelectrophoresis. In addition to bimetallic rods, similar movement has been observed by the authors in systems of gold and silver colloids that are assembled in solution into heterodoublets.\(^8\)

The electron flux from one metal into the other is an essential part of the autoelectrophoretic movement. If the metals are not in electrical contact, the individual peroxide decomposition half-reactions cannot selectively occur on each metal; this lack of a reaction dipole prevents proton transport through solution and therefore autoelectrophoresis does not occur. This observation led to the initial goal of this work: using a semiconductor particle as a photoresistor between the two metals in a bimetallic peroxide motor. This would allow for control of the electron flux (and therefore particle motility) using incident light. Indeed, the authors have fabricated three-component metal-semiconductor-metal trimers in the past, (specifically, gold-silicon-silver), but the high native conductivity of silicon prevented these trimers from responding to light.\(^9\)

CdS looked to be an excellent semiconductor for use in our motor systems: it has a very low solubility ($< 10^{-7}$ M\(^{10}\)), a bandgap of 2.4 eV and therefore low native conductivity but still visible-light-responsive, and can be synthesized or purchased as a micron-sized powder. In fact, CdS is one of the most common and simple semiconductors used as a photoresistor. Through its use in our motor assemblies, however, we have observed complex autoelectro- and autodiffusiophoretic movement that suggest the CdS is actively participating in the electrochemical processes, either through direct interaction with electrochemical species or though indirect photodiodic effects with one or both of the metal components. In this work, we demonstrate a variety of metal-CdS motor systems that respond to blue light, both with and
without presence of hydrogen peroxide. It is only through observation of many different motor
assembles that we can gain a full understanding of the fundamental processes taking place that
drive the autonomous motion.

7.2 Experimental & Materials

7.2.1 Materials:

Gold and silver microparticles were synthesized using the recipe developed by Goia and
Matijevic\textsuperscript{11}. The cationic polyelectrolyte poly(allylamine hydrochloride) (PAH, Mw 70,000),
silver nitrate for colloidal silver synthesis, CdS micropowder (1 μm), L-ascorbic acid, gum
Arabic and potassium chloride (KCl) were purchased from Sigma-Aldrich Chemicals, USA. To
synthesize the gold particles, gold chloride (HAuCl\textsubscript{4}) was purchased from Strem Chemicals.
Deionized (DI) water used in all aqueous solutions came from a Millipore Corporation MilliQ
system, with specific resistance greater than 1 MΩ.cm (due to equilibration with CO\textsubscript{2} in air).
Hydrogen peroxide, filter papers, and glassware were obtained from VWR International.
Monodisperse 19 nm sulfate-functionalized polystyrene latex nanoparticles (2% w/v) and 1.4 μm
sulfate-functionalized microspheres (4% w/v) were purchased from Interfacial Dynamics
Corporation (Portland, OR). Monodisperse 1.0 μm silica microspheres (10% w/v) were
purchased from Bangs Laboratories.

7.2.2 Instrumentation:

The optical microscopy images were obtained on a Nikon Eclipse TE2000-U inverted
optical microscope. High-intensity blue light was injected into the sample using a mercury arc
lamp and a Nikon B-2E/C filter cube with excitation wavelengths of 465-495 nm, and a cutoff wavelength of 505 nm. A Sorvall Biofuge Primo Centrifuge from Kendro Laboratory Products was employed, and it was equipped with a swing-bucket rotor. The Ultrasonicator was from VWR International (model 550T).

7.2.3 Two-Component Motor Fabrication

Because the CdS surface has little to no zeta potential in solution below pH 7\textsuperscript{12}, we can form CdS-X heterodoublets using the procedure outlined in Chapter 6 for the fabrication of PSL-calcium carbonate heterodoublets. A solution was prepared with CdS microparticles (volume fraction $\phi = 0.001$), and the other material ($\phi = 0.001$), and in the presence of 10 mM KCl salt was allowed to aggregate for 15 min. Then, a solution of 20 μM sodium polystyrene sulfonate was added to the particles, quenching the aggregation by adsorbing to and giving the calcium carbonate particles a negative surface charge. The solution of stable aggregates, which included CdS-X heterodoublets was rinsed, resuspended in DI water, and observed using optical microscopy on bare glass substrates.

7.2.4 Three Component Motor Fabrication

Trimers of Au-CdS-Ag and Au-SiO\textsubscript{2}-Ag were fabricated using the QEA technique as outlined in Chapter 5. Stock solutions of each type of particle used for assembly were prepared. Core particles used included PAH-functionalized CdS and SiO\textsubscript{2} (volume fraction 0.0005) Satellite particles were gold (volume fraction 0.001) and silver (volume fraction 0.001). The satellite particles were added to a solution of suspended core particles in a test tube, along with enough 30 mM KCl to give a final solution ionic strength of 25 mM. These test tubes were placed on a
roller for 10-20 minutes, and the aggregation was quenched at the calculated time by adding 2 µL of stock 20 nm sulfate-functionalized PSL nanoparticles (volume fraction 0.01). The solution was then diluted by adding DI water, and the resulting structures characterized by optical microscopy.

7.2.5 Optical Microscopy / Blue Light Stimulation of Motor Assemblies

Optical microscopy images and video were taken of each motor assembly, in both DI water and in a 0.1% solution of hydrogen peroxide, in a glass-bottomed petri dish. Motor surface fractions were kept well below 0.001, to keep bubble nucleation at a minimum and reduce the number of motor-motor flowfield interactions. Tracer particles were added, 1.4 µm sulfated polystyrene, to each solution to better see the flowfields. To expose the sample to the high-intensity blue light, the fluorescent lamp shutter was closed, the appropriate neutral density filters were put into place (see section 7.3), the correct filter cube was selected, and the shutter was opened. Movement observations were made both immediately and after prolonged exposure to each intensity of light. One important thing to note is that only the immediate viewing area is exposed to light, as the fluorescent lamp is exposed to the sample through the objective.

7.3 Results and Discussion

7.3.1 Autoelectro- and Autodiffusiophoretic Flowfields

Understanding the movement of the various motor assemblies studied in this work requires an understanding of the electrokinetic processes at work (Figure 7.1). In autoelectrophoresis, the movement of protons from one end of the motor to the other generates an electric field. The electric field lines have a dipole shape. The electric field is strongest near to
the motor surface; this drives the movement of fluid surrounding the motor (as well as at any charged substrate near to the motor). Inert, charged particles near to the motor may move in response to this electric field, but the effect is highly localized.

In autodiffusiophoresis, a stream of ions is generated at one end of the motor. The concentration profile and resulting electric field from this ionic gradient is isotropically outward, driving flows across a much larger region of the fluid. It has been shown that anisotropy of an autodiffusiophoretic motor within its generated concentration gradient is necessary for directed motion.⁴

Several different CdS / metal motor systems were made using simple, in-solution assembly techniques⁸,⁹ previously developed by our lab. Table 1 shows what motors were made, and in what systems they were tested, whether they were motile in the absence of intense illumination, and a qualitative description of their sensitivity to blue light.

The first important observation that can be made from the experiments is the absence of any significant light – induced movement in the samples that did not contain CdS. This suggests that there is very little UV light passing into our sample from our light source, as the silver-silica doublet motors would have shown a strong response to UV light⁴. Secondly, the response of all samples (regardless of the presence of hydrogen peroxide) containing Ag-CdS contacts to the highest intensity of incident blue light demonstrates that CdS is not performing solely as a photoresistor in our assemblies; instead, it is somehow working with the silver to generate solution gradients that drive motion.
Figure 7.1: Autoelectrophoretic (a) and autodiffusiophoretic (b) field lines surrounding a three-component motor. In the autoelectrophoresis case, the electric field is localized, resulting in a motor that only affects the movement of fluid or other particles that are near to its surface. In the autodiffusiophoresis case, the field lines spread outward from the motor into solution, affecting large regions of the system.

7.3.2 Flowfield Mechanics of Three Selected Motors

To understand better the behavior of these light-responsive motors, three samples were analyzed in-depth. First, a gold-silver heteroaggregate motor in 0.1% peroxide from Chapter 4 was examined (Figure 7.2a). These motors move in a directed fashion. The tracer particles tend to gather at one end of the motor (in this case, the leading end), and there is a slight exclusion region of tracers opposite. These regions are well defined and hold fast; they are not consistent with particles being dragged along due to simple hydrodynamics. From this system we can deduce that that tracer anisotropy around the moving motor is the flowfield characteristic to autoelectrophoresis (and indeed, this is consistent with Figure 7.1a).

The second sample examined is Figure 7.2b, Doubt-1NP, doublet and higher order aggregate motors of CdS & Ag particles in DI water. As explained in the Experimental section, the CdS is functionalized first with a cationic polyelectrolyte (PAH), and upon electrostatic
attachment to the negatively charged silver particles, is ‘quenched’ using a negatively charged latex nanoparticle (containing a sulfate functionalization). Therefore, the actual CdS – Ag doublet contains a both amine and sulfate groups near the metal – semiconductor junction.

The fluorescent lamp used to expose the motor sample to high intensity blue light has two neutral-density filters that transmit 25% and 15% of the incoming light, respectively. This allows for 5 levels of light exposure: off, 3.75%, 15%, 25%, and 100% of the maximum. In the CdS-Ag motor system in DI water, no movement was observed without light exposure, and little movement was observed until 100% intensity. Tracer studies of the CdS-Ag system (Figure 7.2b) show the tracers forming strong exclusion regions around each motor, indicative of an autodiffusiophoretic mechanism (and consistent with Figure 7.1b).

Table 7.1 Motor Systems Fabricated Using In-Solution Assembly.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Particle 1</th>
<th>Particle 2</th>
<th>Particle 3 (if applicable)</th>
<th>Peroxide Conc. (% vol)</th>
<th>Initial Movement?</th>
<th>Light Responsiveness?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sil-1P</td>
<td>CdS</td>
<td>Silica</td>
<td>---</td>
<td>0.1</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Sil-1NP</td>
<td>CdS</td>
<td>Silica</td>
<td>---</td>
<td>---</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Sil-2P</td>
<td>Ag</td>
<td>Silica</td>
<td>---</td>
<td>0.1</td>
<td>Some</td>
<td>Slight</td>
</tr>
<tr>
<td>Sil-2NP</td>
<td>Ag</td>
<td>Silica</td>
<td>---</td>
<td>---</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Sil-3P</td>
<td>Ag</td>
<td>Silica</td>
<td>Au</td>
<td>0.1</td>
<td>Slight</td>
<td>None</td>
</tr>
<tr>
<td>Sil-3NP</td>
<td>Ag</td>
<td>Silica</td>
<td>Au</td>
<td>---</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Doub-1P</td>
<td>Ag</td>
<td>CdS</td>
<td>---</td>
<td>0.1</td>
<td>Some</td>
<td>Strong</td>
</tr>
<tr>
<td>Doub-1NP</td>
<td>Ag</td>
<td>CdS</td>
<td>---</td>
<td>---</td>
<td>None</td>
<td>Moderate</td>
</tr>
<tr>
<td>Doub-2P</td>
<td>Au</td>
<td>CdS</td>
<td>---</td>
<td>0.1</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Doub-2NP</td>
<td>Au</td>
<td>CdS</td>
<td>---</td>
<td>---</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Tri-P</td>
<td>Au</td>
<td>CdS</td>
<td>Ag</td>
<td>0.1</td>
<td>Slight</td>
<td>Strong</td>
</tr>
<tr>
<td>Tri-NP</td>
<td>Au</td>
<td>CdS</td>
<td>Ag</td>
<td>---</td>
<td>None</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
The most interesting result to us is the response of the third examined sample, Tri-P, a Au-CdS-Ag trimer motor in 0.1% peroxide. Initially, there was practically no movement observed in the absence of applied blue light. At low light intensities (3% - 25% intensity), the trimer motors showed directed motion in the sample, with tracer rich / exclusion regions identical to those seen in the Au-Ag peroxide case, i.e., autoelectrophoretic flowfields (Figure 7.2c).
However, at the highest blue light intensity (100%), the trimer motors began to move very quickly until they inevitably adhered to the glass after a short time. Throughout this movement, as well as after, tracer particles streamed away from the motor (Figure 7.2d). This flowfield looks very similar to the Doub-1NP sample (7.2b), suggesting a transition from an autoelectrophoretic to an autodiffusiophoretic flow mechanism at the higher light intensity. Indeed, the tracer rich / exclusion region is maintained during the first few seconds of the new motion. After this time, however, the tracers break away from the motor surface and are pushed out with the others.

The Au-CdS-Ag trimer motors in peroxide and blue light appear to be active using two different mechanisms of action, depending on light intensity. At lower intensities, the CdS acts as a photoresistor, throttling electron flow from the gold to the silver, allowing for directed autoelectrophoretic motion due to peroxide decomposition. At higher light intensities, the CdS-silver junction begins some sort of photochemical reaction or catalysis (remember, these junctions are active in and out of peroxide). This motion is autodiffusiophoretic in nature and is powerful enough to overcome and mask out the lower-intensity mechanism.

7.3.3 Reaction Identification and Future Experiments

While we can get a good sense of the type of movement the trimer motors in this chapter exhibit by observing flowfields using tracer particles, determining the cause of that movement is much more difficult. The photoresistive mechanism is a reasonable assumption for the lower-intensity movement, but we are not sure what reaction is causing the diffusiophoretic gradient at higher light intensities, both in and out of peroxide. SEM analysis of the silver and CdS surfaces before and after light exposure as well as gas evolution and solution pH tests should help
determine the source of the ions; these experiments are in progress and will be added to this document/my defense soon.

7.4 Conclusion

At low to moderate light intensities, the gold-CdS-silver trimer motor seems to be functioning as designed: the CdS acts as a photoresistor that throttles electron transport. In the absence of light, the motor is ‘off.’ With an increase in blue light intensity, the motor begins to gradually increase its speed. However, at the highest intensities, a secondary mechanism is occurring due to the presence of silver-CdS junctions that changes the characteristics of the motor movement. Exploration of this mechanism is essential to the full understanding of our system, and experiments to accomplish this are ongoing.

One exciting thought is that the CdS is acting as a conduit for electrons (or electron holes) into the silver, which normally needs UV light to be photoactive. Perhaps the CdS is acting like a dye molecule in a dye-sensitized solar cell, converting lower energy into usable electric potential inside the motor. This is a potentially big discovery, as it raises the level of complexity in the particles we can fabricate, giving us more flexibility to create functional, active assemblies
7.5 Acknowledgements

Chapter 6 is a modified version of the manuscript:

Joseph J. McDermott, Tso-Yi Chiang, Nicholas Karkar, & Darrell Velegol.

Photoactive Noble Metal-Semiconductor Trimer Motors In preparation.

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7.6 References


Chapter 8

Conclusions and Future Work

8.1 Research Goals: a Retrospective

At the start of this dissertation, I listed five research goals, driven by the motivating factors of the commercialization of colloidal assembly and the chemical engineering process design, fabrication, and purification of a complex & functional colloidal assembly. At the end of this work, externally controllable, photoactive, three-component catalytic trimer motors were fabricated using a generalized, scalable assembly technique. Additionally, the resulting assembly, a gold-cadmium sulfide-silver trimer, displayed additional mechanisms of action than predicted, including what was possibly a ‘dye-sensitized’ silver photochemical reaction.

I hope it is clear how flexible and generalized the Quenched Electrostatic Assembly technique is. After rejecting silicon as a poor photore sistive material in Chapter 5, I was able to substitute cadmium sulfide microspheres – which was smaller and had a completely different shape and surface functionality – into my trimer assemblies with very little effort. Similarly, the calcium carbonate heterodoublet motors featured in Chapter 6 were easily made using a modified form of the QEA technique.

The only drawback to ‘statistical’ assembly techniques such as SQF and QEA is the resulting distribution of product particles, including singlets of the component particles and higher order aggregates. However, preliminary results from Chapter 3 suggest, at least, that there are thermodynamic ways to separate distributions of particles and assemblies. This will be discussed further in the future work.
Revisiting the research goals, it is clear how the work done in this dissertation satisfies those goals:

1) **Assemble a ‘traditional’ bimetallic catalytic motor from component metal microparticles, and assess its motility in hydrogen peroxide.**

Gold-silver heterodoublets were synthesized using the SQF technique, found to be thermodynamically and mechanically stable, and were active in hydrogen peroxide, moving similar to the bimetallic nanorods previously produced (Chapter 4).

2) **Work to analyze the movement of assembled motors and surrounding particles owing to localized, self-generated electroosmotic and diffusioosmotic flowfields.**

Electroosmotic and –phoretic flowfields were studied in Chapter 4 and Chapter 7, by examining the movement of the bimetallic heterodoublet motors mentioned in goal (1). Diffusioosmotic and –phoretic flowfields were studied in Chapter 6, by examining the dissolution and diffusion of mineral systems into non-equilibrium aqueous solutions. In Chapter 7, these flowfields are juxtaposed, showing how two very similar movement mechanisms for motors in solution can have drastically different flow patterns.

3) **Craft a generalized, flexible assembly technique that allows for the fabrication of three-component, ordered ‘trimer’ particles.**

The Quenched Electrostatic Assembly technique developed in Chapter 5 has proven to be a very versatile technique for producing ordered trimes out of polymer, oxide, semiconductor and metallic particles with varying sizes and surface functionalities.
4) With the knowledge gained from goals (1) and (2), and the assembly technique developed in goal (3), design and fabricate a three-component, photoactive catalytic motor.

In Chapter 7, gold-CdS-silver trimer motors were fabricated using the QEA technique. These motors were found to be strongly photorresponsive to blue light in the presence of hydrogen peroxide, with little to no motility until light exposure. The fabrication process was made easy by the flexibility of the QEA technique, and due to operation in the visible spectrum, the resulting assembly has opened the doors for many new photosensitive applications for catalytic motors.

5) Explore separation techniques capable of separating colloidal particles by size, shape, or other distinguishing factors that take advantage of the singular complexities of concentrated distributions of colloids.

In Chapter 3, Effective Density Sorting was applied to bimodal and other distributions of concentrated colloidal suspensions to separate particles of different sizes and densities. Rather than be a hindrance, the complex fluid behavior of concentrated colloidal suspensions was a contributor in the mechanistic of separation. This is the only research goal that has gone somewhat unfinished; while there is theoretical evidence for thermodynamic separations based on particle shape and packing behavior, no empirical evidence of such separations was demonstrated, in large part due to difficult diffusion dynamics of oddly-shaped particles within the packed sediment.

The main contribution of this work to the field of colloidal assembly was the design and fabrication of a complex and functional colloidal assembly using a new, generalized assembly technique. By approaching the assembly process as a chemical engineering process, the design, fabrication, and separation of the final product each led to new results and techniques with an
emphasis on scalable, general and flexible processes that can be applied to many systems in the future.

8.2 Future Work

There are three concepts and ideas arising from this work, in particular, that I feel have rich and detailed research futures. First, the complexity of self-generated motors and pumps in this document is well beyond much of the previous work, and certainly beyond our current capabilities to analyze deterministically. Second, while the groundwork is laid within this dissertation for separations of distributions of particles using effective density sorting, the technique is in its infancy and must be applied to increasingly complex systems. Finally, the prospect of diffusiophoretic flows in mineral systems is particularly attractive because of the difficulty of using pressure driven flows in microporous systems.

8.2.1 Crafting ‘Intelligent’ Motors

One of the advantages of self-propelled micromotors is that they can be engineered to change the local environment. For example, in Chapter 6, the CaCO$_3$-PSL heterodoublet motor leaves a trail of dissolved Ca$^{2+}$, HCO$_3^-$ and OH$^-$ ions in its wake. This change in environment not only affects local inert particles, it may affect other motors in the area by changing the local bath concentration, or even the surface charges of substrates. Similarly, combinations of diffusiophoretic motors that release ions that can precipitate new particles when the gradients meet allows for a large degree of flexibility within the system. Photoactive motors can respond to patterns or flashes of light, perhaps by releasing ions that trigger other events. This idea of cascading reactions that drive local osmotic flows can lead to emergent behavior of collections of
these particles. One clear avenue to further the work of this dissertation is determining in what ways individual and collective motors can interact with and react to each other.

On the other side of things, by integrating the complex mechanics of, for example, the gold-CdS-silver trimer motor into simple motor systems, we can add levels of control to that motor system, perhaps even solving the biggest problem with directed motion: Brownian rotation.

### 8.2.2 Effective Density Sorting of Colloidal Aggregates and Continuous Distributions

The simplest effective density sorting experiments are finished. We know bi- and multimodal size and density distributions of spherical colloidal particles can be sorted based on gravitational potential. However, the sorting technique will be especially valuable if it can accomplish one of two tasks: sorting colloidal aggregates (doublets, triplets, etc) from single particles, which would be immediately useful for purifying simple colloidal assemblies; or, sorting continuous size distributions of particles in such a way that the polydispersity of various portions of the sediment are decreased. This second task is relevant not just to colloidal assembly but to any company or lab wishing to purify a monodisperse sample of a high-value colloid.

Additionally, effective density sorting of particles with various shapes is intriguing, because it may reveal valuable results about the physics of 3D, mobile packed configurations of shapes. Interparticle forces are also easily studied using effective density sorting, because particle interaction distances are highly relevant to the final sediment configuration.

There are many elementary steps to take next with regards to the effective density sorting, but I believe the ultimate direction for the research need to be heading for a high-throughput separation technique that is flexible enough to be employed in the purification of many different colloidal assemblies.
8.2.3 Engineering Flows in Mineral Systems

Geologic systems, such as in oil shale, are porous, but it is often difficult to get proper penetration of nanoparticles or fluids into these porous structures using pressure driven flows. Because movement from electro- and diffusio- osmotic flows generates a slip velocity on charged walls, it is much easier to drive flows in narrow channels using electrokinetics than pressure.

Additionally, these mineral systems are already ripe for manipulation, as they tend to contain partially soluble materials, such as gypsum and limestone. The dissolution of these minerals can produce strong electric fields that are localized to the wall surfaces.

In a lab environment, it would be interesting to engineerin complex flowfields by surface zeta potential patterning. By patterning surfaces with different zeta potentials through particle deposition, micropatterned templates or e-beam lithography, the flowfields generated at those surfaces in the presence of electric fields or ionic gradients can be carefully directed and controlled. This will hopefully lead to a better understanding of how to optimize transport of micro- and nano- particles (and emulsion droplets) in to – and out of - more complex geologic systems.
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Publications, Presentations & Patents
Publications
- McDermott, Joseph J.; Chiang, Tso-Yi; Karkar, Nicholas; Velegol, Darrell. “Photoactive Noble Metal-Semiconductor Trimer Motors” In preparation.
- Gonzalez Serrano, Cesar; McDermott, Joseph J. (Corresponding Author); Velegol, Darrell. “Sediments of Soft Spheres Arraigned by Effective Density.” Accepted by Nature Materials (2011).

Conference Presentations
- McDermott, Joseph J.; Chaturvedi, Neetu; Velegol, Darrell; “Quenched Electrostatic Assembly of Photoactive Electrophoretic Trimer Motors” AICHE National Meeting (Nov. 2011)
- McDermott, Joseph J.; Gonzalez Serrano, Cesar; and Velegol, Darrell; “Effective Density Sorting of Soft Colloidal Spheres” AICHE National Meeting (Nov. 2011)

Patents

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