Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of $250 for UW-Madison chemistry Ph.D. candidates.

Wisconsin Initiative for
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The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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Chemical Transformations of Lithium Cobalt Oxide Nanoparticles in Model Environmental Systems

By

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Chapter I. An introduction for non-scientists: Lithium cobalt oxide nanoparticles and how they interact with phosphate molecules

This chapter is accessible to the public through the Wisconsin Initiative for Science Literacy (WISL).

I.0. Context.

Throughout my training in graduate school, I have become increasingly fascinated by the way that we communicate science. One of the most important goals of science and research is to protect and improve the lives of everyone. Science belongs to all of us, and yet, it is not always perceived this way. Scientists can be viewed as elite, untouchable, and our work is often shrouded from the public eye. Even when the public has access to the work, it is often filled with jargon and technical terms, making it entirely inaccessible. This not only is unfair to the public, but it is also a failure of our responsibility as scientists. I believe the mark of a truly good scientist is being able to not only do good science, but be able to boil it down to the most important information, and explain the core of the work in a way that is accessible to anyone. Doing this well is sometimes harder than doing the work itself. As a scientist, you must truly understand your work to be able to communicate it effectively and generally. It is a skill that is important to develop, and the only way to do so is to practice. I’m grateful to the Wisconsin Initiative for Science Literacy at UW-Madison for providing this platform for researchers at our institution, and for sponsoring and supporting the creation of this chapter.

I.1. Introduction to nanomaterials.

In 1959, physicist Dr. Richard Feynman delivered a lecture entitled "There's Plenty of Room at the Bottom." In Feynman's lecture, he posed the question, "what if you could fit the entire Encyclopedia Britannica on the head of a pin?" He painted a picture of a world where you could "swallow the surgeon," "arrange atoms the way we want." While at the time, the speech felt more like science fiction than science itself, many of his predictions are well on their way to becoming reality.

The core message of Feynman's lecture was the idea that there is a whole world of science and technology yet to be discovered, that we could access by zooming in, or looking down. Many credit this lecture with sparking the field of nanotechnology, though the field did not truly take off until the 1980s.

What is nanotechnology? Simply put, nanotechnology is the study of nanomaterials that have a technologically relevant function. Nanomaterials, as the name suggests, are very, very small materials. These materials can be technologically useful, because the properties of many materials change when you shrink them down to the nanoscale.

Just how small are we talking, you may be wondering. One nanometer is one billionth of a meter (a meter is just about the same as one yard, or 3 feet long). Figure I.1 illustrates what a nanometer is with respect to some other materials. Note that one nanometer is smaller than a single cell - bacteria cells can be about 1,000 nm long, with human cells being larger at around 10,000 nm long. A period at the end of a sentence in 12-point type is about one million nanometers long, and a tennis ball is around one hundred million nanometers long. Something this size is really hard to conceptualize, but the important thing to know is that nanomaterials are really, really small.

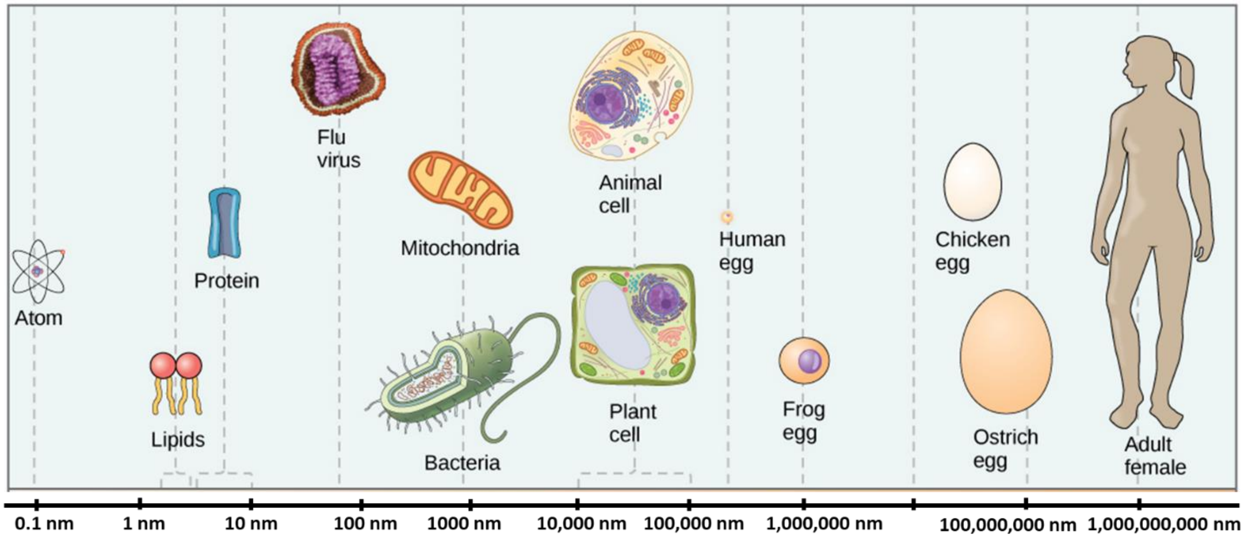

Figure I.1. Scale of different objects in nanometers. Image from WikiCommons.

When you take a bulk material and shrink it to the nanoscale, the properties of that material start to change. Take gold nanoparticles for instance. Nanoparticles of gold can be suspended in water, meaning that they are so small they can essentially "float" in water. An example of this in everyday life is muddy water – the dirt is suspended in the water, and so the water appears to be brown. When gold nanoparticles are suspended in water, the water appears red. Figure I.2 shows suspensions of gold nanoparticles in vials, where the larger the particle size, the darker the red color. This is unlike bulk gold, which has a color we are all familiar with. The color changes because on the nanoscale, the gold interacts differently with light. Below each vial in Figure I.2 is a microscopy image of the gold nanoparticles.

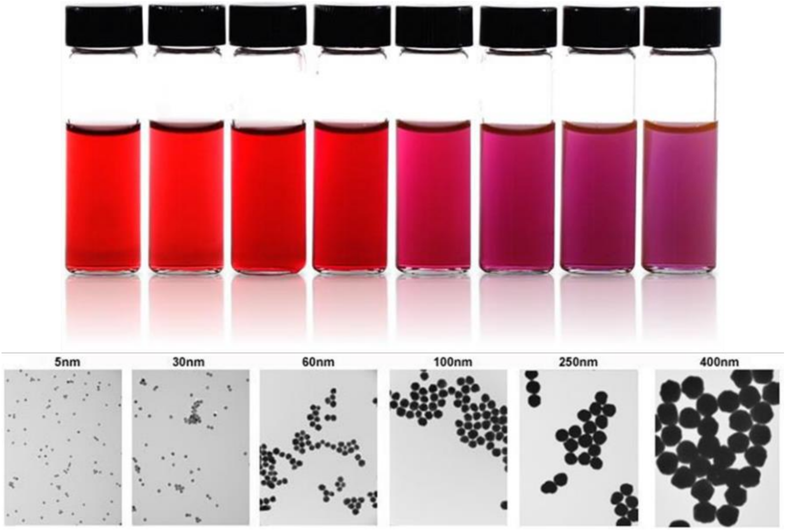

Figure I.2. Top: vials of gold nanoparticle suspensions. Image from Shopify. Bottom: microscopy images of the nanoparticles that are in each suspension. Image from Sigma Aldrich.

Another example of how the optical properties of nanomaterials is different from the properties of the bulk material is illustrated in Figure I.3. Thin films of silicon dioxide (SiO_2, or quartz), have very different visible colors depending on their thickness in the nanometer-range. The 300 nm thick film of quartz is a vibrant purple, while the 200 nm film is a sunny yellow. Both are vastly different from the bulk crystal, shown on the right.

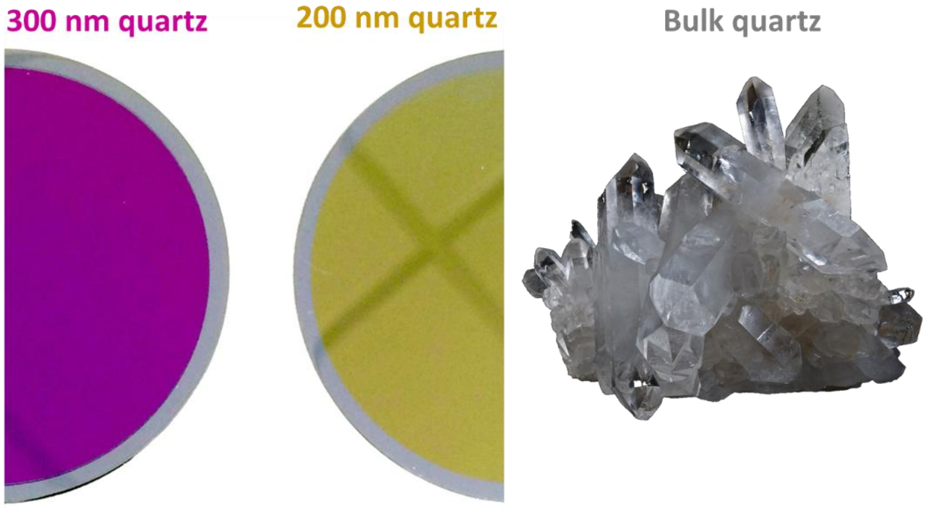

Figure I.3. 300 nm of quartz is purple (left) while 200 nm is yellow (middle). Bulk quartz crystal is transparent. Image from WikiCommons.

The color of a material is just one example of a property that changes on the nanoscale. One reason that nanomaterials have different properties than their bulk counterparts has to do with the surface area to volume ratio of the atoms in the material. As you take a material and shrink it down, there is a higher percentage of the total atoms in the material that are at the surface. We can consider Rubik's cubes of different sizes to understand how this works. Figure I.4 shows four different sizes of Rubik's cubes. The volume of a 5 by 5 by 5 Rubik's cube is 125 units cubed (length times width times height) and the surface area is 150 units squared (area of each face of the cube, 5 times 5, multiplied by the number of faces, 6). Therefore the surface area to volume ratio is 1.2.

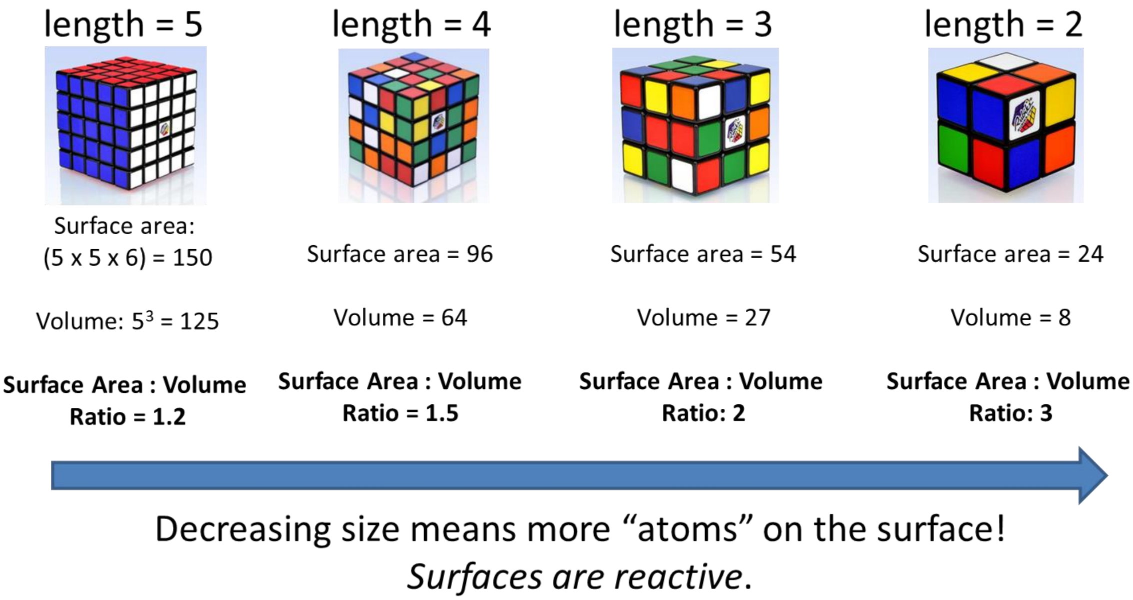

Figure I.4. Illustrating the surface area to volume ratio using Rubik's cubes. Images from Rubik's.

If we shrink this cube down, by the time we have a 2 by 2 by 2 cube, we now have a surface area of 24 units squared, and a volume of 8 units cubes. Our surface area to volume ratio is now 3, which is much higher than the 5 by 5 by 5 cube. The reason this is important for materials is that surface atoms are often more reactive. The more atoms at the surface, or the higher the surface area to volume ratio, the more reactive a material can be.

I.2. Introduction to sustainable nanotechnology.

Because nanomaterials have such interesting properties, researchers have been using them to create new technologies. One example of this is a particular kind of nanoparticle called quantum dots, which can have vibrant and varied colors. These types of nanoparticles are being used in tablet and television screens, such as QLED TVs. Scientists are also researching how nanomaterials can be used to advance science, energy storage, solar panels, and much more.

But because there is still a lot that we don't know about nanomaterials, a lot of scientists have dedicated their studies to understanding the potential environmental and biological impacts of nanomaterials. My research is part of the Center for Sustainable Nanotechnology (CSN), funded by the National Science Foundation, which is a collaborative network of scientists from many fields dedicated to understanding the fundamental chemistry behind how nanomaterials interact with biological and environmental systems. Some of our scientists study how nanoparticles and bacterial cells interact – Figure 5 shows an electron microscopy image of gold nanoparticles at the cell wall of a bacterium.[1]

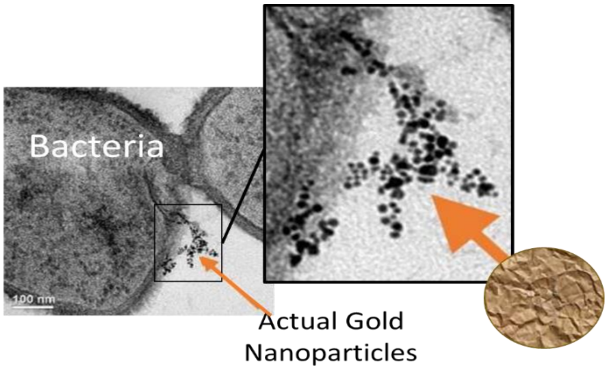

Figure I.5. An electron microscopy image of gold nanoparticles near the surface of a bacterium. Adapted from Reference 1.

We also have scientists studying nanomaterials for sustainable agriculture, where we've shown that copper containing nanomaterials can help fend off fungal disease on watermelon plants.[2] My thesis research is a part of the CSN, where I have spent five years in graduate school researching how a particular nanomaterial called lithium cobalt oxide interacts with model (simplified) environmental waters, which I will explain in more detail below.

I.3. What is lithium cobalt oxide, and why do we care about it?

Lithium cobalt oxide (LCO) is a very important material in all of our lives. It is a material that is used in lithium-ion batteries (LIBs), which are the most common type of rechargeable batteries. LIBs are in our cellphones, laptops, Nintendo Switch systems, and more; most things that you plug in to recharge are not only LIBs, they also contain LCO or a related material.

LIBs have three main components; the anode, the cathode, and the electrolyte, as shown in Figure I.6.[3] LIBs operate by shuttling lithium ions between the anode and cathode through the electrolyte. The electrolyte is a combination of a solvent and a salt that are able to solvate the lithium ions. This solvation is effectively like providing a boat for the lithium ions to travel through the liquid from the anode to the cathode. For each lithium ion that is transferred, an electron can move through a circuit, which generates electricity. A common anode material is graphite, which is a layered version of carbon (the same thing that is used in pencils). LCO is a popular choice as a cathode material, as it consists of layers of oxygen and metal atoms, with lithium "intercalated" in between the layers. What that means is that the lithium ions are able to be very mobile, which is a good quality for a battery cathode, since the function of the battery relies on those lithium ions being able to move easily from anode to cathode, and vice versa. The structure of LCO makes the movement of lithium ions easier, by providing a straight, short path for them to follow to get to the "boat" (electrolyte) and travel to the anode.

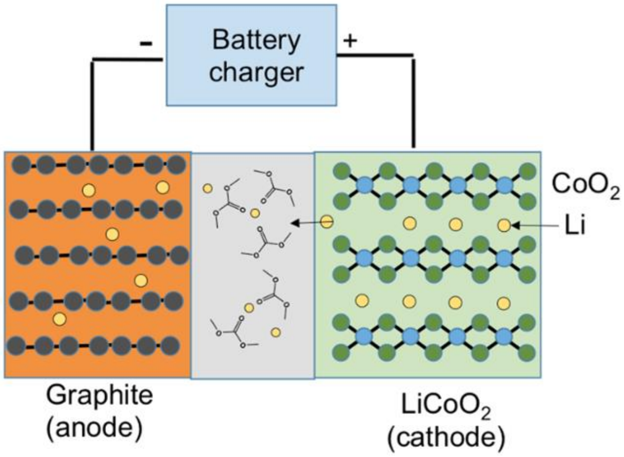

Figure I.6. Schematic of a lithium ion battery. Image from Bob Hamers (adapted from Ref 3)

It's undeniable that these materials are ubiquitous in our every-day life. Many of us have cell phones, laptops, rechargeable wireless headphones, portable gaming systems – almost everything you use that you plug in to charge at night uses a battery like this. LIBs are being used in electric vehicles, the production and use of which is on the rise. In just one of these vehicles, there are tens of kilograms of cathode material. With no federally instated infrastructure for recycling these materials, and low economic incentive to do so, it is inevitable that these materials will be improperly disposed of and end up in landfills and potentially our environment. For these reasons, researchers like me in the CSN are working to understand what the impacts of these materials like LCO may be on the environment.

I.4. How does lithium cobalt oxide interact with the environment?

"The environment" is a very complex system, and it is an oversimplification to lump it all into one category. For the sake of this chapter, the environment that I am considering is surface waters, like those of lakes or rivers. Cathode materials being disposed of may end up in these systems through a variety of pathways. Cathode materials like LCO function well in their intended systems – batteries – which require a very specific chemical environment to operate. These materials are not designed to be in water, and until recently, we did not know what would happen to these materials if they were put into water. Surface waters can have a variety of different molecules in them that could interact with the LCO particles, as suggested schematically in Figure I.7. When LCO interacts with these molecules, the particles may "transform" – an umbrella term we use to describe a change in properties of the material from their "pristine" or intended form.

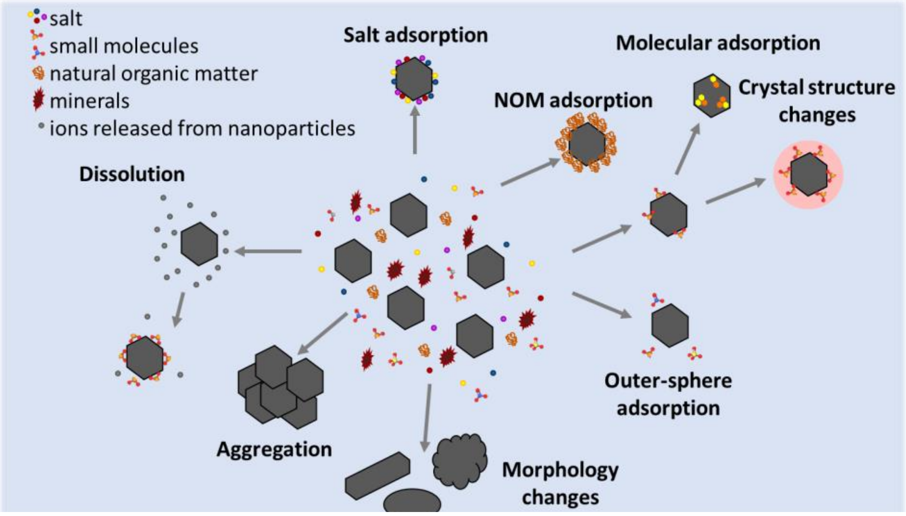

Figure I.7. Possible transformations of LCO nanoparticles in a natural water system.

A lot of my work has focused on one small aspect of this – looking at how LCO interacts with a molecule called phosphate. Phosphate is an important molecule that is environmentally, biologically, and technologically relevant. Phosphate is present in surface waters, such as those in lakes, at low concentrations. Many places are seeing enhanced concentrations of phosphate in their surface waters, as a result of fertilizer runoff. Fertilizer runoff occurs when some of the applied fertilizer doesn't make it to the intended plants; instead, this excess fertilizer is transported from the soil into these bodies of water. Excess phosphate in natural waters can have negative effects.

High phosphate environments support algae, and so the algal blooms that you may see on the lakes in Madison during the summer are caused in part by phenomena such as this.

Phosphate is also important in biological systems. It is present in the growth medium that researchers in the CSN use to grow the bacteria they study. It is important for us to know if LCO and phosphate interact, and how that may change how LCO then interacts with the bacteria. Phosphate groups are also present in many biomolecules, such as DNA. Phosphate coatings are also used on medical implants to help recognition between the implant and the body, and similar coatings are used on pipes for irrigation to prevent metal leaching into the water.

I used an analytical method known as infrared spectroscopy to investigate how phosphate and LCO interact. Infrared spectroscopy is a useful technique that provides specific signatures for every molecule. When a molecule interacts with infrared (low energy) light, the chemical bonds in that molecule can stretch or bend. These motions are caused by an absorption of the energy by the molecule, which results in a signal that we can read. We can think of the bonds between atoms as springs that can be stretched and compressed. Certain bonds will be like stiffer springs, and so more energy will be needed to stretch and compress those bonds. Because every bond requires a specific amount of energy to be stretched or compressed, we can use this technique to identify what those different bonds are.

I specifically used a surface-sensitive method of this technique that let me see how phosphate molecules bind to LCO.[4] Figure I.8a shows a schematic for my experimental set-up. I deposited LCO nanoparticles on the surface of a prism, which I could then seal in a liquid cell. I was able to then flow phosphate over the particles, and see if and how it stuck to the surface. I found that phosphate binds to LCO quite strongly, and even after trying to rinse it off, it stays bound. By interpreting the infrared spectroscopy signature shown in Figure I.8b, I was able to determine how the molecule was bound to the surface, shown in Figure I.8c. This allowed me to hypothesize that LCO with phosphate bound to it would likely be negatively charged, because how the molecule was bound left a negative charge on the molecule. To test this hypothesis, I used another technique to measure how the nanoparticle's zeta potential, or effective surface charge, changed in the presence of phosphate.

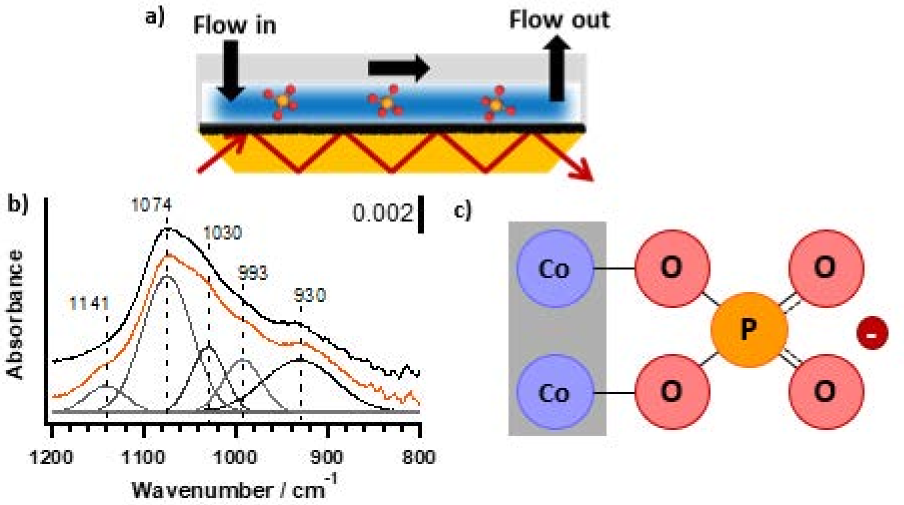

Figure I.8. a) a schematic of the infrared spectroscopy experimental setup. The binding of phosphate to LCO is probed by flowing phosphate solutions over a surface with LCO particles on it. b) the infrared signature from the experiment, adapted from Reference 4. c) the proposed structure of phosphate bound to the LCO surface.

When I measured the zeta potential of LCO in different concentrations of phosphate, I found that my hypothesis was correct. Figure I.9a. shows that as phosphate concentration increased, the LCO particles became more and more negatively charged. At the highest concentrations, the particles had zeta potentials of -30 millivolts (mV) or lower, which is consistent with particles being stable in suspension – similar to how the gold nanoparticles in Figure I.2. are evenly dispersed within the liquid. I used another spectroscopic technique to get more evidence for this phenomenon. The particles themselves absorb light in the near-UV range of the color spectrum. Absorbance is proportional to concentration, so by tracking LCO absorbance over time, I was able to get a sense of what percentage of particles were stable in suspension. We can use the "muddy water" analogy again to picture what this looks like. If you added mud to water and shook it, it would form a suspension, and the water would appear brown. Over time, the dirt would settle to the bottom, and the water itself would look less and less brown. This means less light is being absorbed, and more is being reflected. That's exactly what I was tracking for the LCO particles, but instead of just looking by eye, I used the instrument to provide more exact data on how the absorbance was changing over time. Figure I.9b shows how the absorbance of the LCO suspension decays over time more quickly when phosphate isn't present (blue trace) than when it is present (orange trace). This means that the LCO settles to the bottom quicker when phosphate is not there. Because absorbance is proportional to concentration, this confirms that in the presence of phosphate, the LCO is more stable in suspension, as the zeta potential measurements suggested.

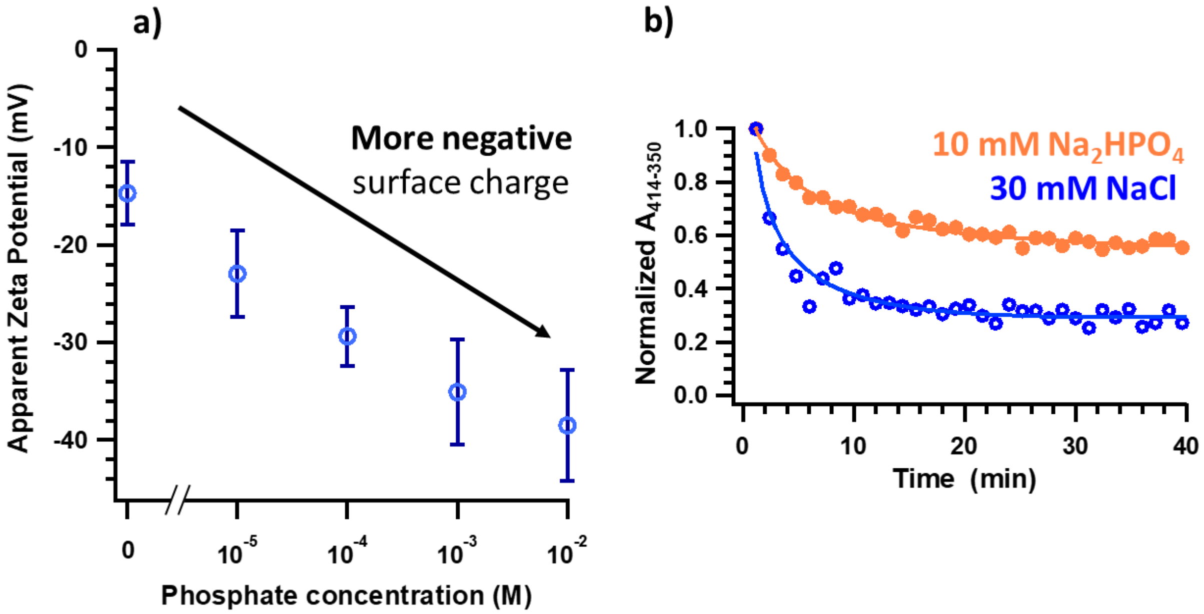

Figure I.9. a) zeta potential measurements of LCO in phosphate. b) UV-visible spectroscopy absorbance of LCO in suspension over time. Figure adapted from Reference 4.

I.5. Summary and perspective.

While this study was done on a simple model system, these results point to some important factors to consider when trying to predict and understand nanoparticle fate and transport in the environment. This study shows that molecules adsorbing, or sticking, to LCO, can change the properties of the nanoparticle. In this case, phosphate adsorption changed the surface properties by making the charge more negative, which made the particles more stable in suspension. This may impact bioavailability of particles in environmental systems. If they are staying in suspension for longer times when phosphate is present, this may dictate if and how they encounter different organisms. For instance, phosphate adsorption may make LCO more accessible to surface water dwellers, such as fish. Studies by my collaborators have seen that LCO can enter fish gill cells and have negative impacts on their health.

Phosphate isn't present in every surface water system, and so researchers in the CSN are also studying how LCO impacts bottom-feeders such as chironomids, which are a type of fly that, as it's growing, lives in soil. It's important for us to gain an understanding of how LCO can impact environmental systems from every level – from the chemistry side, as I've presented here, and from a more biological side, which my coworkers study. Together, we in the Center for Sustainable Nanotechnology hope to use our combined knowledge and research findings to aid in the safe use and disposal of nanomaterials.

I.6. References.

1. Feng, Z. V.; Gunsolus, I. L.; Qiu, T. A.; Hurley, K. R.; Nyberg, L. H.; Frew, H.; Johnson, K. P.; Vartanian, A. M.; Jacob, L. M.; Lohse, S. E.; Torelli, M. D.; Hamers, R. J.; Murphy, C. J.; Haynes, C. L., Impacts of gold nanoparticle charge and ligand type on surface binding and toxicity to Gram-negative and Gram-positive bacteria. *Chem Sci* **2015,** *6* (9), 5186-5196.

2. Borgatta, J.; Ma, C.; Hudson-Smith, N.; Elmer, W.; Plaza Pérez, C. D.; De La Torre-Roche, R.; Zuverza-Mena, N.; Haynes, C. L.; White, J. C.; Hamers, R. J., Copper Based Nanomaterials Suppress Root Fungal Disease in Watermelon (Citrullus lanatus): Role of Particle Morphology, Composition and Dissolution Behavior. *ACS Sustainable Chemistry & Engineering* **2018,** *6* (11), 14847-14856.

3. Hamers, R.J., What's With All Those Flaming Cell Phones? A Primer on Battery Safety. In *Sustainable-Nano*, Sustainable-Nano, Ed. Sustainable-Nano: 2016; Vol. 2020.

4. Laudadio, E. D.; Bennett, J. W.; Green, C. M.; Mason, S. E.; Hamers, R. J., Impact of Phosphate Adsorption on Complex Cobalt Oxide Nanoparticle Dispersibility in Aqueous Media. *Environ. Sci. Technol.* **2018,** *52*, 10186-10195.