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## **Redox Properties of Silver Nanoparticles**

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Abstract:

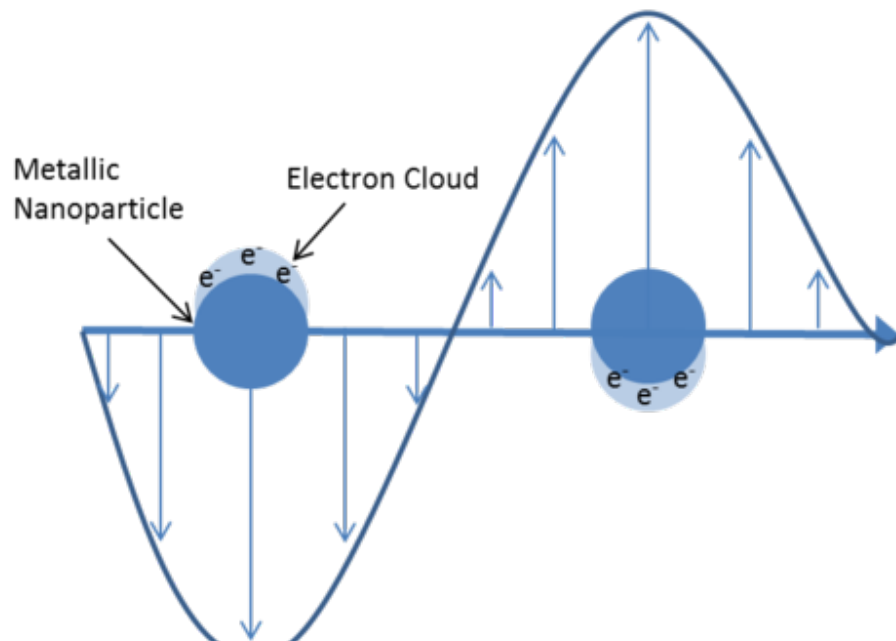
In this study, we use cyclic voltammetry to measure how nanoparticles would affect the redox potential of various electron transfer mediators (ETMs). The main class of ETMs tested was quinones, and the working electrode was decorated with gold nanoparticles. ETMs are major players in regulating redox processes in aquatic environments, and contamination of these aquatic systems with nanoparticles could drastically change these redox processes. To see if there is a difference in redox potential, we compared redox potentials between bare glassy carbon electrode, indium tin oxide (ITO) electrodes with a polycyclic aromatic hydrocarbon (PAH) layer, which was used to attach nanoparticles, and indium tin oxide electrodes with both PAH and gold nanoparticles. We find that on bare glassy carbon electrode, the redox potential was -0.005 V, ITO electrode with PAH surface had a redox potential of -0.004 V and an ITO electrode with PAH and gold nanoparticles had a redox potential of -0.067 V. As each layer is added, electrocatalysis increases and redox processes become more reversible, showing that gold nanoparticles have an electrocatalytic effect on ETMs.

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Nanoparticles exist in many facets of everyday life, yet, we never notice them. On clothes, silver nanoparticles act as anti-microbial agents, fighting bacteria and keeping our clothes clean. In most batteries, nanoparticles improve energy efficiency and battery longevity. They can even be used in certain cleaning products, improving a products ability to remove stains. Why are these nano-materials so widespread in everyday life? It's because when certain chemicals such as silver or gold are reduced to infinitesimally small sizes (anywhere from 10-

300 nm), their properties change from their bulk form. In their normal form, silver and gold are rare metals, usually worn as jewelry or used in electronics as conductors. But when they are in these smaller sizes, their properties and appearance changes. For instance, bulk silver has the a polished metal appearance resembling a shiny grey. In their nanoparticle form, silver spheres take the color of an olive green. Manipulations of size or shape of the nanoparticle can further change their color, spanning all the colors of the rainbow. For instance, when we create silver prisms instead of silver spheres, every color of the rainbow can now be created in nanoparticle form (Grundl et al. 2011).

Nanoparticles are also capable of Localized-Surface Plasmon Resonance (LSPR). This unique phenomenon describes the oscillation of electron clouds of nanoparticles in response to an electric field. In other words, the electrons of nanoparticles move back and forth when an electric field is applied.



**Figure 1.** A graphic illustrating the unique LSPR properties of nanoparticles.

This unique process is what differentiates a nanoparticle from its bulk form, giving it properties that allow for applications in sensing, as well as useful everyday activities. As with other properties of nanoparticles, the LSPR effect can be manipulated when changing nanoparticle size and shape. This property also allows nanoparticles to both absorb and scatter light. While large, normal objects usually just absorb light, nanoparticles do both. While this can also improve sensing techniques in chemical analysis, it also allows nanoparticles to sometimes have two colors at the same time. When light is directly shined at some nanoparticles, it will show one color, and when it is left alone, it will have a different one (Anker et al. 2008).

Another important property of nanoparticles is their role in redox chemistry or the exchange of electrons. Redox chemistry is a fundamental piece of life: it allows us to breathe in oxygen and make energy, it allows plants to create energy from the sun, it allows bacteria to naturally clean the water on Earth. Without the exchange of electrons, life would not exist. In redox chemistry, there are 3 general parts: the species that gains electrons, the species that loses electrons and the mediator or the species that helps shuttle electrons from one species to the other. In every redox reaction, these 3 parts are present, and without these 3 parts, redox would not happen. However, electrons are not just exchanged spontaneously; there must be a potential or voltage reached in order for redox to occur. This point is called the redox potential, the point where electrons are either given or received (Bastus et al. 2014). Every reaction between 2 species has its own unique redox potential. If a potential is very high, the reaction requires a high voltage in order to occur. If a potential is very low, the reaction only needs a low

voltage. Through natural processes, nature has generally stabilized these redox processes, allowing life processes to occur without disruption.

However, due to the omnipresence of nanoparticles, it has become increasingly possible for these nanoparticles to enter our natural environment, especially into our aquatic systems (Levard et al. 2012). Toxic factory waste, improper battery removal or even simply washing our clothes in the washing machine are all potential methods of bringing nanoparticles to the environment. Since nanoparticles have properties of LSPR and many of them come from a family of strong conductors (gold and silver), there are possibilities that these nanoparticles are affecting and changing the redox processes in our environment. Specifically, nanoparticles may be adjusting the redox potentials of vital reactions, making species unable to exchange electrons (Bastus et al. 2014) When electrons are not being transported, the overall process may shut down and the environment could be thrown into disarray.

One of the most likely mechanisms for how nanoparticles may change redox potentials are via the mediators or electron transfer mediators (ETMs). ETMs are abundant in aquatic redox systems and are vital parts to shuttling electrons between two species. They also are major determiners in the redox potential of a reaction. If nanoparticles somehow interact with ETMs, either via a redox reaction or via binding or some other method, than the redox potential could be changed (Buscher et al. 2002). Changing the redox potential of the ETM may make a process much less likely to occur, potentially damaging the aquatic environment.

Due to the growing threat of nanoparticle pollution, my research attempts to quantify the redox processes of nanoparticles and ETMs and from that data, determine if they pose a threat to the natural redox processes that occur every day. As we already know, ETMs function

based on a redox potential, which determines how much voltage is needed to shuttle electrons. The important piece to the puzzle is that redox potential. By measuring the redox potential in variable situations involving nanoparticles, we can determine how the redox potential is changing in response to nanoparticles. We can also make predictions about how nanoparticles are interacting with ETMs and what type of nanoparticles are most dangerous.

The main approach to determine if the redox potential changes is by utilizing cyclic voltammetry. This method utilizes a potentiostat which applies a variable voltage while measuring current. It applies a voltage and measures current on an electrochemical cell: a tiny 10 mL cell with 3 electrodes. Inside this cell are two major components: the working electrode and the electrolyte solution. The working electrode is where the reactions take place while all other electrodes allow for measurements of potential and current. The electrolyte solution is where we will add chemicals or analytes to test the potential. Redox reactions between electrolyte and working electrode work at the surface of the working electrode as electrons are passed back and forth (Dobre et al. 2014).



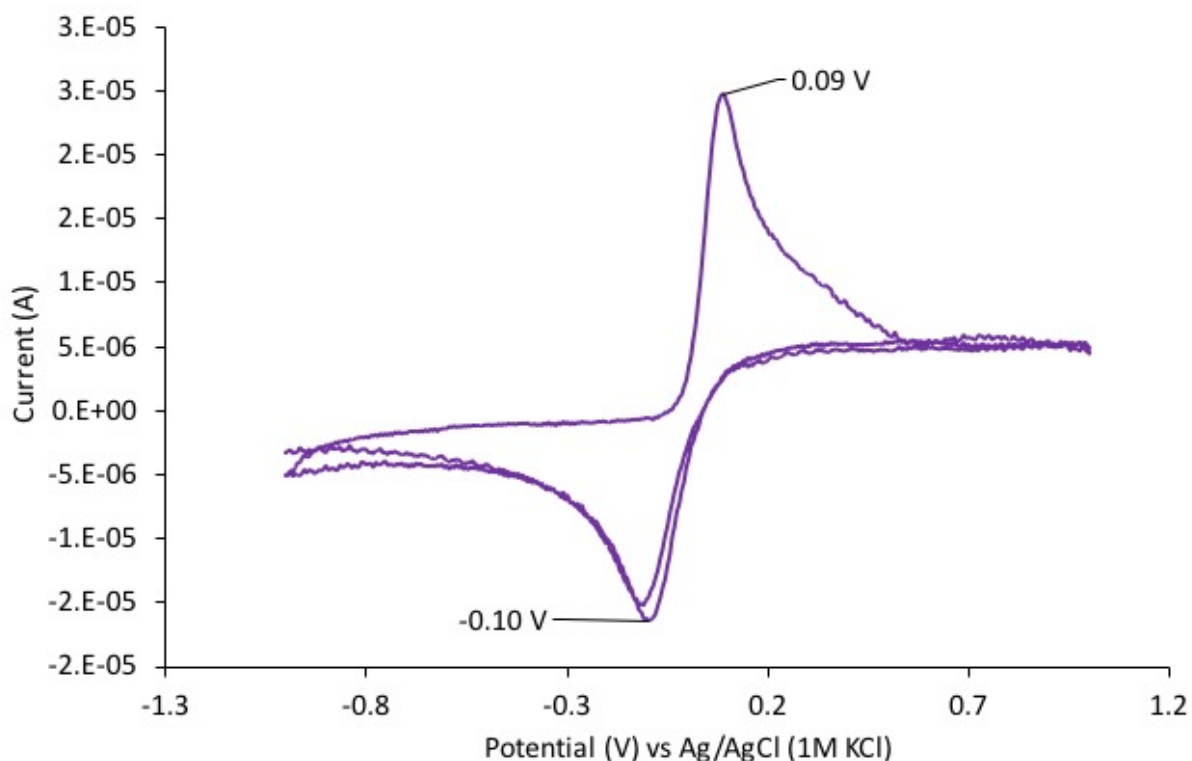
**Figure 2.** An electrolytic cell that is fully set up with the 3 electrodes immersed in electrolyte solution. Nearly all CV experiments were set up in this cell.

To simulate real aquatic environments, we also plan to test different nanoparticle pollution scenarios. Essentially, there are 3 different possibilities: nanoparticles bind or attach to the ETMs, nanoparticles float in solution with the ETMs and nanoparticles bind or attach to another surface in the aquatic environment. In order to test these scenarios, we must use an indium-tin oxide electrode, a non-traditional, glass-based electrode that allows for attachment of nanoparticles.

Another key component is the use of UV-Vis spectrometry. In this technique, absorbance and wavelength of light of the nanoparticles is measured. Since the nanoparticles we use have distinct colors, we can track how the colors shift during cyclic voltammetry. We can also track its concentration since absorbance is proportional to concentration. Any new peaks will also signify new species that may be created. In simultaneously using UV-Vis spectrometry and cyclic voltammetry, we can determine both the redox potential of various



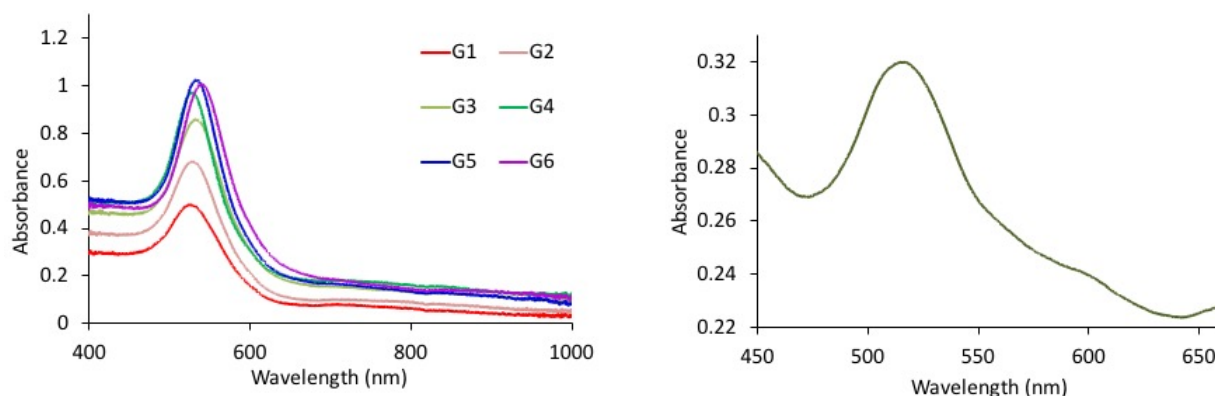
scenarios and track the growth or loss of all reacting chemical species, allowing us to make predictions on the effects of nanoparticles on the concentrations of natural species.



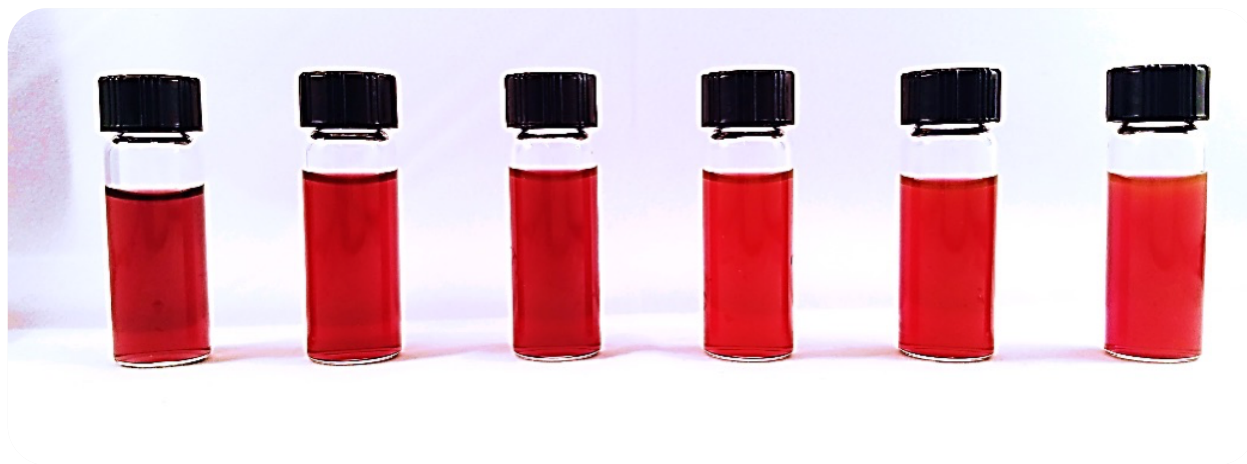
**Figure 2.** Cyclic voltammetry with glassy carbon electrode in 1,2-naphthoquinone-4-sulfonate. Used to determine a baseline redox potential for future comparisons.

Before showing some key results, it's important to understand the important pieces to the data that we collect. The first type of data is of a cyclic voltammetry data where we measured the redox potential. Here, we add an analyte such as an ETM into an electrolyte solution, ramp potential up and down and measure the current. Each peak represents a redox event where positive currents are oxidations and negative currents are reductions. The most important part is where on the x-axis these peaks occur. By averaging the potential at each

peak, we can determine the redox potential of any analyte. Then, we can compare that redox potential in different situations.

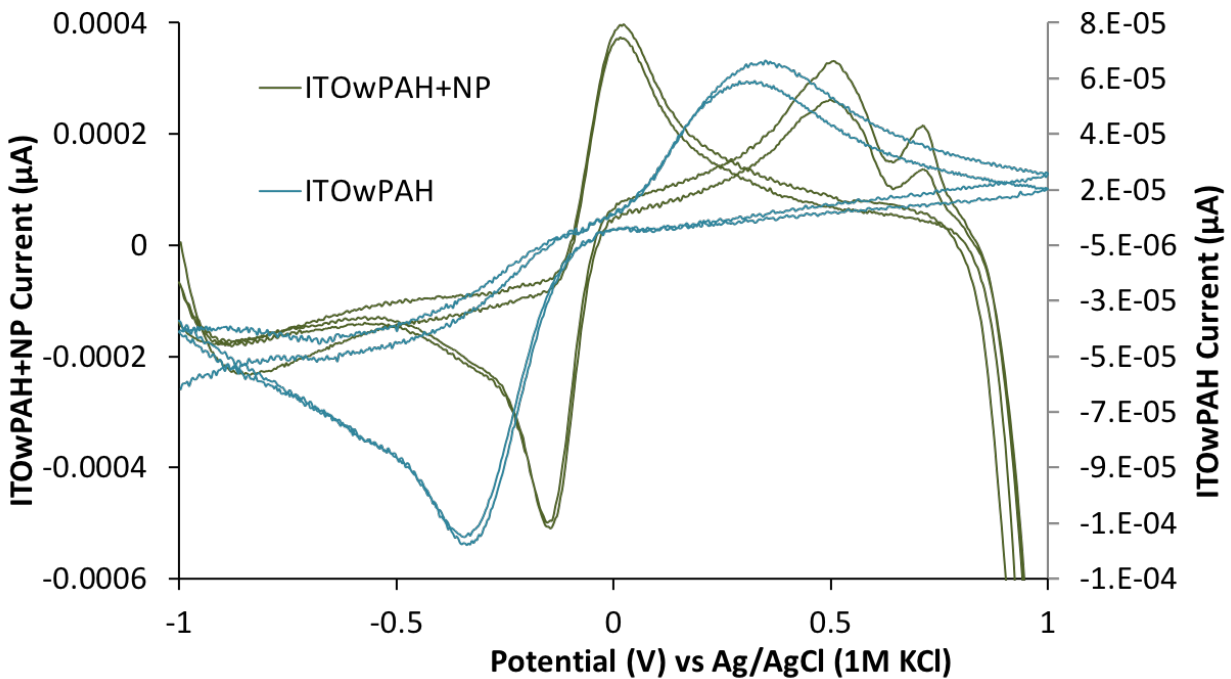


**Figure 3.** Examples of UV-Vis spectra. On the left, spectra of gold nanoparticles at different points during synthesis. On the right, spectra of gold nanoparticles attached to an electrode used for cyclic voltammetry. The main purpose of these types of spectra are to confirm what we synthesized is actually gold nanoparticles and that they were successfully attached onto the electrode.



**Figure 4.** A visual representation of gold nanoparticles. From left to right, nanoparticles grow slightly larger (about 5-10 nm larger per tube). A slight change in color can be noticed in the picture as nanoparticles begin growing in size.

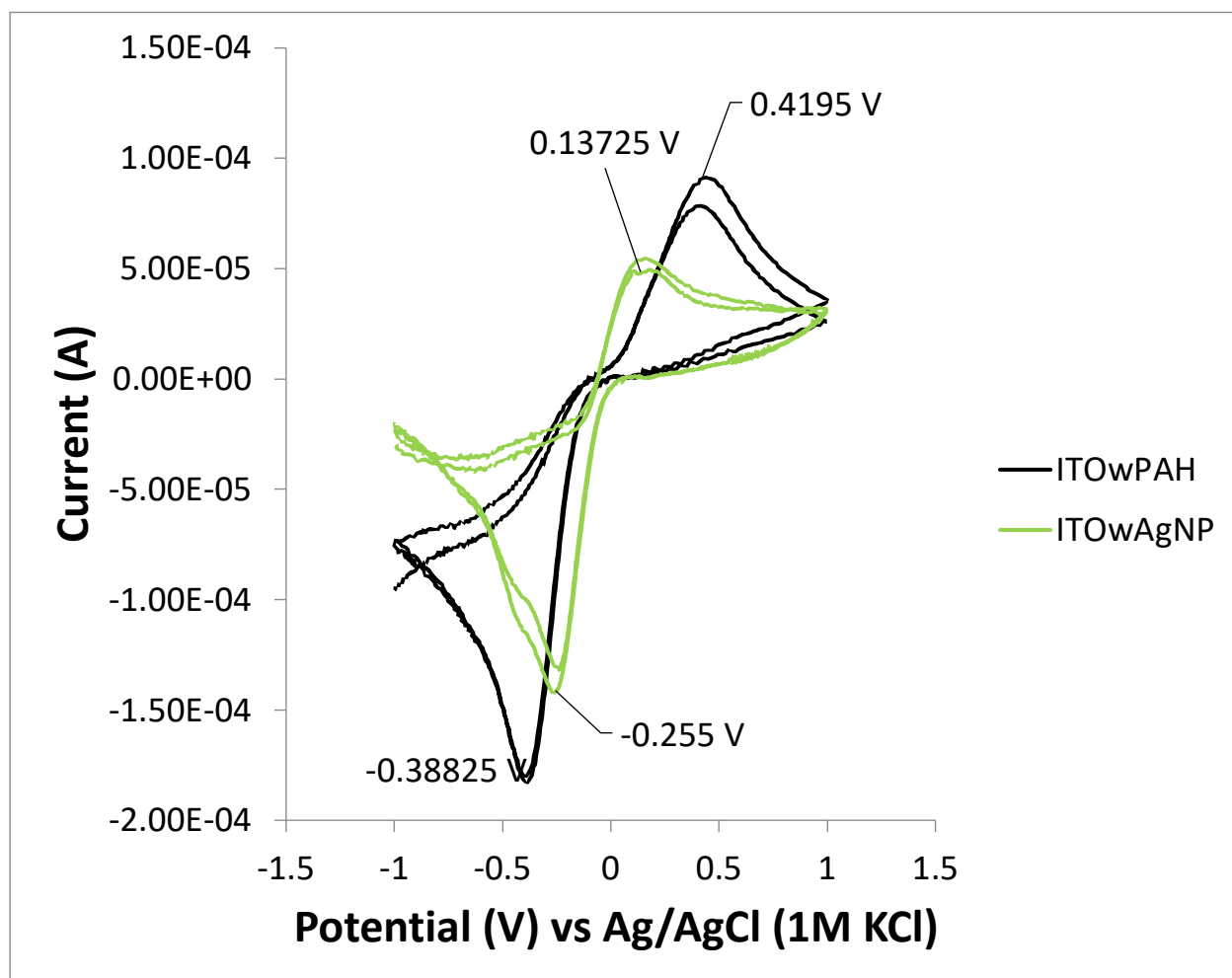
The 2<sup>nd</sup> important type of data is the UV-Vis spectroscopy. The main purpose of this data is to reveal the concentration and confirm the existence of various chemical species. Since most nanoparticles emit a certain color, they also have a certain wavelength where they have a maximum absorbance. For the gold nanoparticles in figure 3, this is approximately 520 nm. We are also able to observe how the gold nanoparticles change during synthesis. From this, we can make predictions about why the nanoparticles are shifting colors, why the nanoparticles are decreasing in concentration/absorbance and determine if new species appear. If new species appear, a new peak would appear in the spectra (Damiane et al. 2008). Ultimately, the goal is to simultaneously take cyclic voltammetry measurements at the same time as UV-Vis spectroscopy measurements. With this combination, we can determine the redox events, chemical reactions and end result of the interactions between ETMs and nanoparticles.



**Figure 5.** Cyclic voltammograms of 1,2-Naphthoquinone 4-Sulfonic Acid in the presence and absence of Au nanoparticles. A scan rate of 25mV/s was used for both scans.

Now that we have a foundational understanding of important data points in CV and UV-Vis data, we can now begin looking at some key findings. Here, we have a cyclic voltammogram of a common ETM (1,2-naphthoquinone-4-sulfonate). The light blue represents a normal indium tin oxide electrode with no gold nanoparticles attached, while the olive green shows the same electrode with nanoparticles attached. Clearly, both redox peaks have shifted significantly closer to each other. Once we average the peaks and determine the redox potentials, we found the redox potential was shifted from -0.005 V to -0.067 V. When potentials are shifted towards more negative numbers, electrons are more easily oxidized and the point at which redox

reactions occur is shifted. We also find that the peaks are much closer to each other, demonstrating higher reversibility of the reaction.



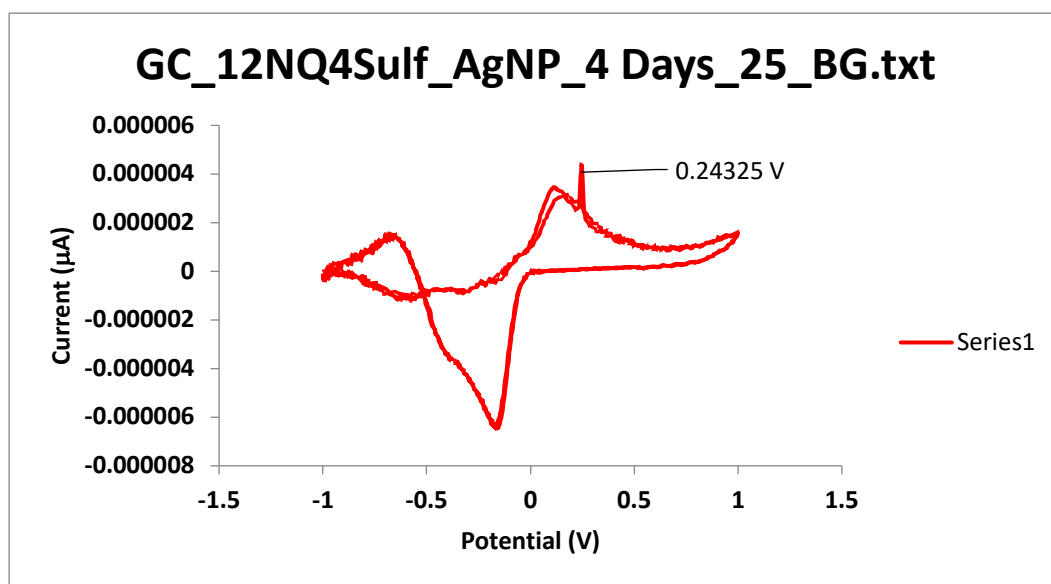
**Figure 6.** Cyclic voltammogram of 1,2-Naphthoquinone 4-Sulfonic Acid in the presence and absence of Ag nanoparticles. A scan rate of 25mV/s was used for both scans.

Using silver colloids, the more common, everyday nanoparticle, yielded similar results.

The attachment of silver nanoparticles changed the redox potential from 0.01513 V to -0.05888 V. Again, we see a shift towards more oxidizable solutions and more reversible redox processes,

further suggesting that the introduction of nanoparticles to aquatic systems may disrupt or change natural redox processes.

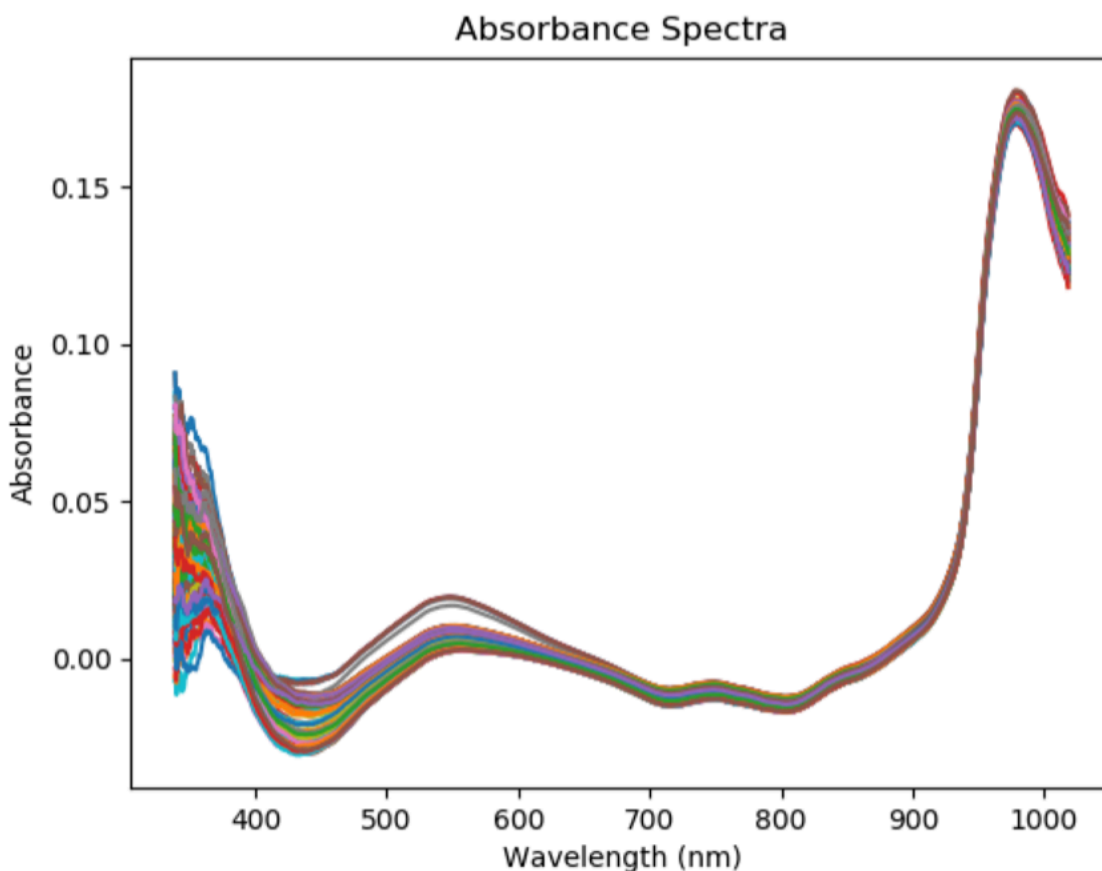
The attachment of nanoparticles onto electrodes simulates one possibility of how nanoparticles would interact with an aquatic system. Another possibility would be nanoparticles in solution with ETMs. In this experiment, rather than attach nanoparticles onto an electrode, both the ETM, nanoparticles and electrolyte solution are allowed to mix and incubate for a variable number of days or weeks. Here, we run into unexpected results.



**Figure 7.** CV of 1,2-napthoquinone-4-sulfonate using a glassy carbon electrode and mixed with silver colloids. Allowed to equilibrate for 4 days.

This CV led to many peaks and bumps that could not really be explained. The crossing at the beginning, the small bumps right before or after a redox event and the inconsistent spikes in current. Although past research has identified possible explanations, there is no way to fully show that what is happening chemically is being shown in the data. Because of this, we started

experimenting with simultaneous UV-Vis spectroscopy in order to confirm and determine what was happening that the surface of the electrode. If the bumps did indicate changes in concentration of analyte, then that should be reflected in the spectra.



**Figure 8.** Absorbance spectra of AgNP (Prisms) in KCl during CV.

This is a UV-Vis spectra taken over the course of a CV. We are measuring the absorbance of the nanoparticles that are attached onto the electrode. A wavelength of about 550 nm shows that silver nanoparticles are on the electrode. The absorbance shows the concentration of nanoparticles, where increased absorbance means increased concentration. By eye, it looks like during a CV, the concentration of silver nanoparticles decreases. However, when analyzing the actual time course of each individual scan, the absorbance actually oscillates back and

forth. It goes from high absorbance, to low absorbance and back again. This correlates with our CV scan: oxidation would oxidize nanoparticles off of the electrode while reduction would add nanoparticles back on. So while it seems to suggest that nanoparticle concentration changes during redox events, it is more difficult to make a simple conclusion as such.

With this first attempt at spectroelectrochemistry, we run into one of our major difficulties: our home-made set-up that limits our experimentation. We used an indium tin oxide electrode connected to a copper wire via a silver epoxy. The problem is that these cells where we are conducting CVs are 1 cm<sup>2</sup> in area and the epoxy can very easily contaminate the solution. Due to the small area, the wires for the counter electrode and alligator clips needed to connect to the instrument are constantly moving and not stable. Any movement during these experiments leads to fluctuations in the results because new molecules will experience redox events on the surface of the electrode. All of this could have potentially led to the oscillating absorbance maximums in figure 8.



**Figure 9.** An ITO (indium-tin-oxide electrode connected to a copper wire. Homemade electrode used as a working electrode for CV experiments.



Another major problem are the un-explainable peaks. In analytical chemistry, understanding every part of a graph is essential to understanding exactly what is happening both physically and chemically. It is not enough to understand that redox events are occurring, but we must seek to understand why or how these un-predictable redox events are occurring. Some previous papers suggest ETMs self-dimerizing or nanoparticles turning into ions and causing spikes in current, but there's no easy way to currently confirm this phenomenon (Giovanni and Pumera 2012). That leaves data such as those in figure 7, where nanoparticles are mixed in solution, difficult to explain and understand. We expected shifts in redox potential in these different experimental set-ups, but instead, we are observing the appearance of new peaks at seemingly random, un-repeatable spots.

Because of the lack of understanding of the chemical reactions occurring on the surface of the electrode, future research should look towards characterizing the properties of silver nanoparticles. By using similar techniques (CV and UV-Vis), we can better understand the redox properties of nanoparticles. Properties such as the redox potential of silver nanoparticles, how the redox potential changes in different environments, how redox potential changes when different types of nanoparticles are used such as different shapes and sizes or how nanoparticles are changing in concentration based on the CV. All of these different types of data determined by CV and UV-Vis can aid in beginning to understand the physical phenomena occurring on the surface of the electrode. And in understanding the surface of the electrode, we can better understand how nanoparticles interact with ETMs in solution. Once we

understand how these two chemical species interact, we can begin to make conclusions on what the data is actually showing us.

An important part of these future studies is the experimental set-up. Up to now, we have been using home-made electrodes, set-ups and home-made software. There are 3 important pieces that make these experiments difficult. In terms of our homemade electrode, we are using indium tin oxide, a transparent electrode that allows for nanoparticle attachment and simultaneous UV-Vis. UV-Vis spectrometry would not work if the electrode was non-transparent. However, ITO is known to have slow electron kinetics with organic substances, meaning that it is much slower at having redox events with natural chemicals like ETMs (Pattadar et al. 2019). Because of this, many CVs with ETMs are much more variable and inconclusive. There is also the difficulty of creating the home-made electrode. As of now, we attach a copper wire to the electrode via a silver epoxy. Although the silver epoxy and copper wire are highly conductive, the silver epoxy can easily contaminate the electrolyte solution, leading to unwanted redox events. As of now, we use hot glue to cover up the epoxy, but leaking may still occur. There is also the possibility of the glue adding extra noise to the UV-Vis. In terms of our set-up, we use instruments from two different companies, making it difficult to coordinate together. Since we want to simultaneously measure CV and UV-Vis, these programs have to be started at the same time and end at the same time. There also has to be a way to match up data points on a time scale. As of now, we use python to insert data and combine it, but the instruments are never truly “in sync”.

Despite its shortcomings, this research project has shown promising results for the future that needs some fine-tuning to acquire data that can be published. Early CVs suggest

that nanoparticles do have the potential to change the redox potential of ETMs, therefore possibly affecting the aquatic redox properties in a natural environment. But more rigorous characterization of the physical processes behind this interaction must be determined before that conclusion can be determined. As we continue to work on this project, more emphasis will be put onto the nanoparticles, as well as improving upon the home-made set-up. We plan to start doing CV and UV-Vis experiments with just the nanoparticles alone, as well as attempt to use different sizes and shapes of nanoparticles. After we have a streamlined set-up, along with a better understanding of the chemical processes of nanoparticles and ETMs, we can begin to draw conclusions about its effect on aquatic redox systems.

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