ADHESION OF SILVER NANOPARTICLES TO GRAPHITE SUBSTRATES

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ADHESION OF SILVER NANOPARTICLES TO GRAPHITE SUBSTRATES

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Abstract

To better understand the life-cycle of a nanoparticle (NP) it is important to study how nanoparticles adhere to substrates. Various removal techniques were used to study the adhesion strength of silver nanoparticles to carbon substrates with different surface chemistries. TEM and IR were used to characterize the NPs and substrate respectively. We developed a qualitative method to determine adhesion strength. A brush is run along the surface and the change in nanoparticle concentration is measured using AAS. Refinement of this process is needed to show a correlation between the force of adhesion and the surface chemistry, namely the determination of surface area of the substrate and precise control over the bristle of the brush.
Acknowledgements

Without the help provided to us from several people, this project would not have been able to achieve its goals. As such, we wish to extend thanks and acknowledgement to these people and groups.

To start, we would like to thank Rose Roy, a MS Material Science student. For her master’s thesis, Ms. Roy developed a method that allows for quantitative analysis of particle adhesion on the nano-level. She did this through use of lateral force microscopy, and demonstrated the need for a macroscopic measurement technique. She also provided assistance with the nanoparticle synthesis methods and obtained the TEM images used in this project.

Next, we thank Donald Pellegrino and Anastasios Gavras for help with the bulk removal process. Mr. Pellegrino provided assistance with the atomic absorption spectrometer, allowing us to determine the change concentration after each force was applied. Mr. Gavras provided assistance with the optical microscope used during the force measurement.

We would also like to thank our advisors, Professors Drew Brodeur (Chemistry), Nancy A. Burnham (Physics), and Jianyu Liang (Mechanical Engineering) for all their assistance. Professor Liang noticed how nano-silver is an excellent antimicrobial, and the importance of understanding the life-cycle of these nanoparticles. Professor Burnham, an AFM expert, provided a program that is able to calibrate lateral force measurements, allowing for the quantitative analysis on the nano-level. Professor Brodeur provided insights on the effects various surface chemistries could have on adhesion strength.

Lastly, we would like to thank the Grant-In-Aid of Research Program from the National Academy of Sciences, administered by Sigma Xi, The Scientific Research Society for their donation to this project.
Executive Summary

Nanoparticles offer unique opportunities in a variety of different applications, ranging from medical and electrical to cosmetics. The global market share for applications involving nanoparticles is set to double in the next four years. With the growth of the field comes a societal concern about the potential release of particles into the environment. Of particular interest to us are silver nanoparticles.

With 10% of the world's population lacking access to potable water—said to increase to 50% by 2035—a cheap and effective method of purification is needed. Silver nanoparticles offer a solution to this problem. Bulk silver has a well-documented antimicrobial ability, which is enhanced on the nano-level. Recent studies have shown that nanoparticles that are adhered to a substrate are extremely efficient at removing harmful bacteria from water sources.

Yet the nanoparticles do not distinguish between harmful bacteria and all other cells, meaning a release of silver nanoparticles into the environment could have negative effects. To mitigate this, an understanding of the adhesion of nanoparticles to a substrate is necessary. Classical microparticle removal techniques, such as centrifuge and flow, are no longer applicable on the nano-level since these processes depend on the magnitude of the particle radius. The development of a bulk removal method for the use on nano-level is discussed in this report.

To test the method, we prepared ten samples by varying the nanoparticle synthesis techniques, the substrate’s surface chemistries, and the deposition practices. The silver nanoparticles were synthesized through chemical reduction and thermal decomposition. The substrate’s surface chemistry was either native graphite, a carboxyl ligand on graphite, or an ethylenediamine ligand on graphite. This was to see if different surface chemistries affected the adhesion of the particle. The nanoparticles were deposited to the surface through two practices,
drop—where the particles are synthesized separately from the substrate—and in-situ synthesis—with the substrate in the reaction vessel. TEM was used to measure the size, distribution, and agglomeration of the nanoparticles. IR was used to confirm the functional group on the substrate.

The process we developed to remove particles from the surface is modeled after a simple cantilever. We moved a bristle along the surface of the substrate, applying a force proportional to the bristle deflection. An optical microscope measured the bristle deflection. This force is able to remove particles from the substrate. The samples were then submerged in 16 M HNO₃. Each liquid sample will have a change in concentration equal to the amount of nanoparticles removed from the surface. The concentration of each liquid sample was measured using Atomic Absorption Spectroscopy (AAS).

The results of the AAS test showed two trends. First, the drop method demonstrates a change in the particle surface concentration as the force on the surface is increased. This suggests a proof of concept, that the bristle method is a way to remove nanoparticles from a surface; however, no quantitative force measurements were collected. The lack of quantitative forces stems from the difficulty in measuring the deflection of the bristle. As the bristle head was moved along the surface, the tip of the bristle would stay in place, and then snap to position once the force on the bristle overcame the static friction. Second, the in-situ method produced inconclusive evidence of a change in the particle concentration.

The inconclusiveness of the in-situ technique is due to the complex surface morphology of the sample. The morphology arises from the functionalization process. The hot acid used attacks the secondary bonds that hold the graphite “sheets” together, replacing them with the desired functional groups. This causes the graphite to partially fall apart, creating a complex and irregular surface. Since the nanoparticles were synthesized on the surface of the substrate, the
particles cover the sample completely. This means that the concentration of silver in the AAS samples is proportional to the total surface area of in-situ samples. Since the drop method only applied particles to the top of the substrate, the change of concentration between samples is consistent with expectations.

The bristle approach provides a strong foundation for a quantitative method of determining adhesion strength of nanoparticles to a substrate. To reach a quantitative level, a few refinements are necessary. Most important is a process to determine the total surface area of the sample, providing a relationship between surface area and solution concentration, normalizing the results. Second is a method that can overcome the static friction problem. Two ways to address this problem could be a device that can move the bristle head across the surface incrementally or using a video camera to record the test. Either of these techniques would allow the displacement to be determined just before the snapping point, leading to accurate force measurements.

The bristle technique provides a maximum force needed to remove silver nanoparticles from a carbon substrate; however, in the applications that involve purifying water, a fatigue limit—the amount of time at a specific force that will remove the nanoparticle from the surface—is also needed. The classical processes for particle removal are more appropriate for this type of measurement. An understanding of both the maximum force and fatigue limit might allow one to adequately determine and predict the life-cycle of silver nanoparticles and create standards that prevent the escape of particles into the environment.
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Chapter 1 Introduction

This project addresses the issue of nanoparticle adhesion to a substrate. It explores the process by which silver nanoparticles adhere to a carbon substrate. The following sections explain what nanotechnology means, what some current problems in the field are, and why silver nanoparticles are an important area of study. Lastly, this chapter provides a brief view of the experimental methods.

1.1 What is Nanotechnology?

The concept of nanotechnology started in a talk by physicist Richard Feynman titled “There’s Plenty of Room at the Bottom” in 1959; however, the term was coined by Professor Nori Taniguchi in the 1981, and popularized by K. Eric Drexler during that decade. The original idea was to develop working machines at the atomic level, literally building gears and motors atom-by-atom. In the three decades since the coining of this term, the concept has grown into a thriving field for both academia and corporate research leading to a great deal of applications. Today, the National Nanotechnology Initiative defines nanotechnology as:

The development at the atomic, molecular, or macromolecular levels using a length scale of approximately one to one hundred nanometers in any dimension; the creation and use of structure, devices and systems that have novel properties and functions because of their small size; and the ability to control or manipulate matter on the atomic scale [1].

Nanoparticles have enhanced chemical and physical properties as compared to their bulk counterparts. This is largely due to the high surface area per unit volume ratio and quantum
effects [1]. These enhanced properties drive the increased use of nanoparticles in modern science and commercial products.

Nanoparticles are characterized into two main groups, natural and anthropogenic (particles that are manufactured or engineered). This is then broken down into organic (carbon containing) and inorganic (non-carbon containing, like silver nanoparticles) [2]. To understand the environmental impact of nanoparticles, both natural and anthropogenic particles need study.

1.2 Problems with Nanoparticles

Due to the relative immaturity and rapid growth of the field, the effects of nanoparticles on the environment are not fully understood. Estimates predict the global production of nano-materials will increase from about 2,000 tons between 2005 and 2010 to almost 60,000 tons between 2011 and 2020 [3]. This, coupled with increased reactivity of nanoparticles, causes a concern about the affect nano-materials will have on the environment.

A number of studies have shown that nanoparticles are easily absorbed into many different mammalian cell types [2]. After absorption, research shows that nanoparticles affect specific parts of the body like the eyes, lungs, and skin [4]. The nanoparticles enter these tissues and react in ways that causes cell death. Current speculation by researchers suggests that nanoparticles’ small sizes allow them to pass through the cell membrane that prevents the bulk counterparts. The body has natural defenses against low concentrations of nanoparticles; however, with their increased use, it is unclear if the body can protect itself against nanoparticles [5].

These experiments demonstrate how nanoparticles are possibly damaging to life; however, it is not known if these experimental results are translatable into environmental effects. Many organizations are establishing research plans to determine the nanoparticles’ effect on
ecology [1] [3]. These efforts are to understand and minimize the risks of nanoparticles. One way of minimizing the risk of nanoparticles is by understanding particle-substrate adhesion. By doing this, it prevents the accidental release of particles into the environment—by improving the adhesion strength—or removing nanoparticles that have already escaped—by reducing the adhesion strength.

1.3 Silver and Silver Nanoparticles

Nanotechnology is a promising new field in modern science. As stated above, nanoparticles have increased reactivity compared to bulk compounds. For example, carbon nanotubes have increased electrical properties and high Young’s modulus with relation to bulk carbon compounds, making them a unique and novel modern material. This trend holds true with silver nanoparticles.

A common application for bulk silver is as an antimicrobial. The first documentation of the practice was in Romans books on medicine. The practice continued through the centuries, most commonly as a skin treatment. The use of a silver wound dressing lasted until the end of World War II. At this time, the introduction of antibiotics replaced silver in wound treatments; however, due to the rise of drug resistant bacteria, silver is reemerging as an effective antimicrobial treatment [6].

The study of silver nanoparticles is an attempt to improve the silver’s antimicrobial effects, leading to an abundance of research in the fields of medicine and biotechnology. Furthermore, applications exist in solar energy, circuits, and wastewater treatment.

However enticing the effects of silver nanoparticles may be, it is important to attempt to minimize their potential effects on the environment. Research shows that silver nanoparticles have a negative effect on a wide range of organisms [7] [8]. Silver nanoparticles have well
documented effects on bacteria and animal cells. Few studies exist that show silvers’ effect on plant cells; however, one study has shown that it can prevent cells from undergoing mitosis, which leads to cell death, and, eventually, plant death [9]

Normally, to prevent the pollution silver nanoparticles, and to improve ease of manipulation, they are adhered to a substrate. The necessary adhesion strength is dependent on the application. For example, the adhesion strength of nanoparticles on a bandage—where the major force is artery pressure—can be much less than the adhesion strength necessary for waste water treatment—where the forces comes from potentially hundreds of gallons of liquid. Determination of the adhesion strength is problematic, however.

1.4 A Lack of Understanding

There is a lack of literature documenting the exact adhesion strength of nanoparticles. Currently the only quantitative measurement method is Atomic Force Microscopy (AFM) attraction measurements [10] [11]. Common methods to determine the adhesion for macroparticles, such as liquid flow, are limited when it comes to nanoparticles.

Flow strength measures the force needed to remove particles from the substrate by flowing water over the compound, while AFM measures the interaction of a single nanoparticle to the surface of the substrate [10] [11]. Each experiment presents its own problems. As explored in Section 4.6, Bulk Removal, nanoparticles’ radii are too small to be influenced by classical bulk removal methods. In addition, AFM technique does not provide information applicable to real life applications, since it only measures the force perpendicular to the substrate. Currently, due to these restrictions, there is no quantitative analysis of the adhesion of nanoparticles to substrates, due to the difficulty in implementation on the nanometer scale [12] [13]. Lateral Force Microscopy (LFM) provides a solution to both these problems by allowing for direct
measurements of particle-substrate adhesion in a way that is applicable to what is expected in normal usage. This method is limited by slow data acquisition; therefore, a qualitative bulk removal method is developed to work in conjunction with the LFM method.

1.5 The Process

This project intends to explore how different particle synthesis methods and substrate chemistry affect the particle-substrate adhesion. A qualitative study of this interaction will use lateral force microscopy (LFM) and a bulk removal method. Transmission electron microscopy (TEM) will characterize the size and morphology of the nanoparticles, while infrared (IR) spectra will characterize the chemistry of functionalized substrates.

To begin this process, silver nanoparticles are synthesized through two techniques, chemical reduction and thermal decomposition. Simultaneously two graphite samples are functionalized, one with a carboxyl group and the other with ethylenediamine. The nanoparticles were deposited to a native graphite sample, as well as both functionalized substrates. Two methods of addition are utilized, a simple drop method and an in situ synthesis of the nanoparticles. LFM and a bulk removal technique described in the Methods chapter will then measure the particle-substrate adhesion force. Figure 1 is a flow chart of the complete experimental procedure.
This project explores a qualitative means to measure the particle-substrate adhesion; specifically how silver nanoparticles bind to three substrates: native graphite, and two differently functionalized graphite samples. In addition, two particle synthesis methods provide 8 nm nanoparticles, with little size distribution, and a lack of agglomeration. The various particle and substrate combinations might lead to an understanding of the adhesion mechanism.

The adhesion between the particle and substrate is due to different forces, such as Van der Waals, electrostatic, or covalent bonds, depending on the adhesion mechanism. The quantification of the interaction between nanoparticles and substrates, allows for improved manipulation of nanoparticles in various devices. In addition, it will improve the understanding of the life cycle of nanoparticles, minimizing their environmental impact.
Following this chapter is the Literature Review that discusses concept of adhesion and classical methods to measure adhesion strength. Lastly, it introduces a new technique that this project uses to address adhesion strength. After the Literature Review, the Methodology Chapter provides a detailed layout of the experimental procedure. The Results and Discussion Chapter follows the Methodology and summarizes the LFM data, while also explaining problems that occur during the synthesis process. The project ends with the Conclusion and Future Work Chapter that summarizes our findings and provides ideas for future research.
Chapter 2 Literature Review

To properly determine the how a particle adheres to a surface, it is important to understand the chemistry and physics behind both the synthesis and adhesion of the nanoparticles. This chapter first exams both top-down and bottom-up methods, showing how a bottom-up method is the most applicable synthesis method for the scope of this project. Next are discussions on functionalization, bond strength, and adhesion. These sections demonstrate the variety of affects that can hold a particle to a surface, and how we aim to manipulate these forces. Lastly are sections on removal techniques, one on the nano-level and the other as a bulk method.

2.1 Synthesis of Silver Nanoparticles

The synthesis of any nanoparticle, a sphere with a diameter between 1 and 100 nanometers, involves the breakdown of a bulk compound or ionic salt, followed by a controlled growth of the nanoparticles. All nanoparticle synthesis techniques fall into one of two overarching categories, top-down synthesis and bottom-up synthesis. In general terms, top-down methods involve the electrochemical decay of some bulk component, such as elemental silver, to make the nanoparticles. In comparison, bottom-up methods utilize an ionic salt, such as silver nitrate, to build the particle atom by atom. Figure 2.1 is a simple representation of the general differences between the top-down and bottom-up methods. To prevent the formation of bulk silver, both methods require the use of capping agents that add to the stability of the nanoparticles by slowing the reaction. Both, top-down and bottom-up, methods have advantages and disadvantages, leading to much debate over which method of synthesis is best. The debate
usually encompasses the areas of cost, particle size, and size distribution. The project intends to use fast and facile methods to synthesize particles between 1-15 nm.

![Diagram of top-down and bottom-up methods](image)

**Figure 2.1:** A generalized representation of how nanoparticles are formed through both the top-down and bottom-up methods. The figure shows how the top-down method involves the breakdown of a bulk component to form the nanoparticles, while the bottom-up method involves the building of nanoparticles from atoms [14].

### 2.1.1 Top-Down Methods

Top-down methods break down a bulk metal into nanoparticles through a variety of mechanisms, such as electrochemical, laser ablation, and microwave irradiation [15] [16] [17] [18]. These methods remove the outer layer of atoms, and due to their increased energy from the removal mechanisms, the atoms then form nanoparticles. A universal disadvantage of top-down methods is the possibility of impurities in the bulk component, which hinder the synthesis of nanoparticles.

One commonly used top-down method is an electrochemical method involving two pieces of bulk counterpart, for this example using bulk silver. A galvanic cell is created by inducing an alternating current between the two pieces of bulk silver while they are in solution, creating one cathode and one anode. The induced current liberates silver ions from the anode, while simultaneously creating hydroxides on the cathode [17]. The hydroxides then act as a reducing agent...
and capping agent on the silver ions to form the silver nanoparticles. The unbalanced electrochemical process is modeled by equations 1 through 3:

\[
Ag \xrightarrow{\text{current}} Ag^+ + e^- \quad (1)
\]

\[
2e^- + 2H_2O \xrightarrow{\text{current}} 2OH^- + H_2 \quad (2)
\]

\[
Ag^+ + OH^- \rightarrow Ag^0 \quad (3)
\]

This process creates nanoparticles between 20 and 30 nm. A workup involving filtration of the solution followed by the addition of hydrogen peroxide creates nanoparticles that are between 7 and 20 nm [17]. This process is one of the most cost-effective methods to synthesize silver nanoparticles; however, it does not create nanoparticles of the proper size for the scope of this project.

Laser ablation is able to create nanoparticles that would suffice for this project. It does this by focusing a high powered laser onto a sample of silver immersed in water. When a laser pulse hits the surface of the silver, nanoparticles are forced off and into solution. The size of the nanoparticles varies with the focus of the laser and with different capping agents present in the solution [19]. The method, however, is costly and requires expertise in the use of the laser. In addition, it the method does not lend itself to in-situ synthesis, since the nanoparticles form before they enter solution.

Since top-down methods involve the removal of material from a surface of a bulk compound, there are a large amount of implications in industry, such as nano-channels and nano-circuits. The problems observed by these two examples—lack of proper particle size, required experience in machinery, or cost—extends to all top-down methods, limiting their use in this project. For that reason, this project will use only bottom-up methods.
2.1.2 Bottom-Up Methods

The bottom-up methods for the synthesis of silver nanoparticles is widely practiced due to low cost and use of common laboratory equipment. The most prevalent synthesis techniques for bottom-up methods involve the reduction of various silver salts, due to their reproducibility, control over particle size, and lack of agglomeration. In addition, this project will investigate a method involving the thermal decomposition of a silver salt, in an attempt to improve the nanoparticle substrate adhesion. Commonly, silver nitrate is the precursor to bottom-up methods due to its low cost and high solubility [20] [21] [22] [23]. As mentioned before, at least a capping agent is necessary to produce the nanoparticles from bottom up methods. Typically, these capping agents are sodium borohydride, citrate, polyvinyl alcohol (PVA), and sodium dodecyl sulfate (SDS) [24].

To synthesize silver nanoparticles through a chemical reduction route one can implement various reducing agents, typically, sodium borohydride, citrate, sugars, and organisms. By utilizing different reagents, it is possible to create nanoparticles with different size and size distribution. For example, a method using sodium borohydride as a reducing agent can create particles between 3 and 10 nm, while one using sugars can create particles between 15 and 25 nm [21] [25]. Most of the reduction methods involve the drop-wise addition of a silver precursor into the reaction vessel containing the reduction and capping agents. Under chemical reduction, formation of silver occurs immediately upon addition to the reducing agent. The formation of nanoparticles only happens when the rate of the reaction is slowed. To slow the reaction, the silver is added drop-wise to the reducing solution. This makes the consistency of the drop rate a problem; therefore, an effort must be made for a consistent drop rate to minimize this effect. The choice of silver nitrate and sodium borohydride as reagents are because they are inexpensive and
synthesize silver nanoparticles consistently. Since sodium borohydride acts as both the capping and reducing agent; only two reagents are used in a one-step method [21].

A second bottom-up approach is through decomposition of a silver precursor. For example, silver oxalate decomposes at 140 °C to form bulk silver and carbon dioxide. Through the addition of a capping agent, it is possible to use the decomposition of silver oxalate to form nanoparticles; the capping agent prevents the silver ions from interacting, leading to the growth of nanoparticles and preventing agglomeration. The energy released from the breaking of the oxalate bonds provides the energy required to form the silver nanoparticles. This process is done under a nitrogen blanket and forms silver nanoparticles of 1-10 nm with little size distribution [16].

2.2 Functionalization of Carbon Substrates

Functionalization is a process that adds functional groups to a substrate. Functional groups are compounds that provide a lone pair such as alcohols, carboxylic acid, amine group, amide groups, and thiol groups, and they allow for the possibility of bonding [23] [26]. By functionalizing a substrate, it is possible to improve its reactivity. It can be difficult to functionalize a surface but it depends largely on the method and materials used.

Figure 2.2 shows how graphite looks and interacts with itself on the molecular level. Graphite is extremely stable, making it a very unreactive compound. Graphite’s stability is limited to each “sheet” that comprises the bulk structure; each sheet is comprised of covalently bonded carbons in a ring structure. Each sheet, however, is held together through weaker pi-bonds [27]. This means that each sheet can be separated relatively easily from each other, but each sheet is too stable to react without functionalization. The pi bonding allows for an area that the functional group can attack and bond to since electrons are not fully incorporated into a bond.
For example, a diamond, which does not have any pi-bonds, would be substantially harder, if not impossible, to functionalize.

Figure 2.2: A three dimensional image of graphite. Graphite is composed of flat sheets of covalently bonded carbons. The figure shows three layers of graphite, the white lines represent the covalent bonds that provided strength to each layer. The black lines represent the pi bonds that keep the layers together [28].

There is an abundance of literature on how to functionalize carbon structures [29] [30]. Some methods to functionalize graphite are with mixture of heated acids, ozone, permanganate, and piranha solution [20] [23] [31]. These all oxidize the carbon, adding carboxyl groups onto the surface, as shown in figure 2.3. The mechanism in which a carboxyl group is added is not fully understood; however, it is based directly on the strength of the oxidizing agent. In addition, after adding carboxyl groups it is possible to continue a chain or branch off the carbon surface [26] [32].
The most common functionalization methods involve heated acids; most commonly, the acids are nitric acid, hydrochloric acid, and a 1:1 mixture of nitric and sulfuric acids. Another method is using a piranha solution, 7:3 sulfuric acid and hydrogen peroxide mixture, which uses its own heat of mixing to provide the necessary energy [30]. After the acid treatment, other reagents allow for the creation of large chains to branch off the surface [26].

To create the branches off the surface the hydroxyl group on the carboxylic acid is substituted via a chloride switch or another large group addition to the carbonyl. Using thionyl chloride will convert the hydroxyl group to a chloride leaving group. This allows a nucleophile to bond to the carbonyl adding a branch chain [23]. Another way of substituting the hydroxyl group is using N-Hydroxysuccinimide (NHS) and Ethyl (dimethylaminopropyl) carbodiimide (EDC) in a mixture with the functionalized substrate. This process allows for the addition of amine substituents [31].

Figure 2.3: Graphite layer functionalized with carbonyls, carboxylic, and hydroxyl groups [33].
2.3 Bond Strengths

The nanoparticle can interact with the surface different ways: of most interest to this project are chemical bonds, electrostatic forces, and Van der Waals interactions. Electrostatic forces happen when one atom on a molecule has strong positive or negative charge; this charge then attracts the opposite charge and is held together through attractive forces. Chemical bonding occurs when an electron directly interacts with multiple atom nuclei. Van der Waals forces are secondary forces that act between two particles. In general, covalent bonds are the strongest, followed by electrostatic forces, leaving Van der Waals as the weakest [34].

Chemical bonds are intermolecular interactions and are generally stronger then the forces around the molecule. Chemical bonds can be broken down into three categories: covalent, ionic, and metallic bonding; however, none of these are ever independent of each other. For example, a covalent bond will have ionic characteristics. Covalent bonding is the sharing of the electron between two atoms. Ionic bonding is the transfer of electrons from one atom to another, creating one is positive atom and one negative atom. Since they are attracted to each other, they bond and form a neutral compound. Metallic bonding is bonding where the electrons are donated to a “sea of electrons,” in which the electrons from each atom are free moving and shared between all the nuclei in the compound [34].

The form of electrostatic bonding of most interest to this project is coordinate complexes. Classically these interactions occur when a metal ion is surrounded by electron donating species. The strength of the complex is related to the coordination number of the metal ion and how many electron donating species are present. It is unclear from the literature how strong the electrostatic forces will be in the nanoparticle-substrate system; however, a common way to adhere
nanoparticles to a surface is by making large branched chains onto a surface of a substrate that contains large amounts of electron donating groups [20].

Van der Waals forces are weak, omnipresent forces between all types of matter. They work through electron displacement. When one atom approaches a second, the fluctuating electrons from one atom repel the electrons on the second, creating two temporary dipoles, which is an attractive arrangement of charges. Each interaction itself is extremely weak; however, van der Waals forces gain strength due to their omnipresence [34]. If neither chemical nor electrostatic bonds form, any remaining adhesion is due to Van der Waals forces.

2.4 Adhesion of Nanoparticles to Substrates

Adhesion of nanoparticles onto a surface is not completely understood. The theory of adhesion is split into two mechanisms, particle adhesion and adhesive adhesion. Particle adhesion is when the force between the molecule and substrate is stronger than other forces around it; for example, if the substrate and the particle were turned upside down nothing falls off because the strength of adhesion is stronger the force of gravity [35]. Figure 2.4 is a Venn diagram comparing Particle and Adhesive theories on adhesion.
The adhesive mechanism is when a particle is caught in a cavity or adsorbed on to a surface and can be lost because of the effects of gravity, i.e. the particle is able to roll out of the cavity. There is overlap with the mechanisms of adhesion but the most important aspects for nanoparticles are Van der Waals forces, mechanical interlocking, chemical bonding, and silver to metal diffusion [35].

Many different techniques are implemented to adhere silver nanoparticles to a substrate, such as UV-radiation, PVA, and in-situ synthesis, where the nanoparticle is synthesized with the substrate in the reaction mixture. These processes intend to improve adhesion by increasing the number of chemical bonds between the particle and substrate [31]. Another method of adhesion is through drop-wise addition of nanoparticles onto the surface to see if the nanoparticles will collide and form bonds with the substrate by adsorption [36].

The adhesion mechanisms for nanoparticles are based off the different techniques to synthesize the nanoparticles and how the substrate is functionalized. The adhesion strength will
change depending on the interaction of the nanoparticle and the substrate. Increasing the number of covalent bonds and electrostatic forces will increase the strength of the adhesion. There has been no study of the actual strength; therefore, there is little understanding in what the adhesion between the surface and nanoparticles is. This project devises a qualitative method to determine this force. Section 3.6, Bulk Removal Technique and Section 3.7, Lateral Force Microscopy, contain detailed descriptions of these processes.

### 2.5 Atomic Force Microscopy

Atomic force microscopy (AFM) maps the topography of a sample by the physical movement of a cantilever [37]. Figure 2.5 shows a schematic of the layout of the scanning apparatus in an AFM, as well as the photodiode. To take the image, a tip attached to a cantilever runs along the surface of the sample, much like how an old-fashioned record player read the grooves on a vinyl record (figure 2.5.A). The tip’s interaction with the surface causes normal and torsional deflection of the cantilever. By reflecting a laser off the cantilever, a photodiode, which is divided into four sections, detects the deflection (figure 2.5.B). The photodiode detects the voltage change as the laser moves along the sensor. Normal deflection of the cantilever corresponds to vertical movement on the photodiode, while torsional deflection corresponds to lateral movement on the photodiode. The change in voltage represents the topography of the surface [38].
AFM allows for the study of the surface in a number of ways beyond a topography image. One of the first, and still a very prevalent form of interaction, is the measurement of the attraction forces as the cantilever approaches and retracts from the surface, or force-curve spectroscopy. This form of measurement is the most prevalent way to measure the adhesion of an object to a substrate. If the object of interest is a nanoparticle, it is commonly attached to the tip of the cantilever [11] [40] [41]. The cantilever is brought to the surface and then slowly removed. Attractive forces hold the tip to the surface during the retraction process, deforming the cantilever until it snaps away from the surface. This type of experiment is called a force-curve measurement. Figure 2.6 shows a force curve associated with the approach and retraction for a cantilever whose stiffness is lower than the strength of the attractive forces on the surface. The figure correlates the force on the cantilever with its displacement from the surface. When
studying adhesion to a surface, the point of interest is when the cantilever “snaps-out” from the surface. At this point, the force applied as the cantilever is pulled from the surface becomes greater than or equal to the force of adhesion to the surface [38]. This measurement, however, only gathers information for adhesion in the normal direction. In comparison, lateral force measurements allow for the analysis of how forces interact with the particle from other directions. This method models how forces would be applied to the nanoparticles in nature, since a force is more likely to hit from the side than be a pulling force directly off the surface.

![Figure 2.6](image_url)

**Figure 2.6:** A representation of a force curve during the approach and retraction of a cantilever to a surface. As the cantilever head is removed from the surface, attractive forces lock the cantilever tip onto the surface outside of its normal contact range. The circled area is the point where the force the AFM head applies to the cantilever is greater than or equal to the strength of attractive force on the surface.

Put simply Lateral Force Microscopy (LFM), or friction force microscopy, measures the torsional deformation of the cantilever as it runs along the surface of the substrate. A measurement taken uses the left and right hemispheres of the photodiode, as opposed to the top and bottom ones (see image 2.3B) [38]. LFM lends itself to the study of tribology and the study
of adhesion [42] [43]. The friction on the sample applies a force to the cantilever tip that opposes the scanning movement. This force causes the torsional deflection of the cantilever. This project uses LFM to determine the adhesion of silver nanoparticles on functionalized substrates. The problem in LFM comes from the difficulty in converting the detected voltage into a force. To do this, various calibrations methods exist.

2.5.1 LFM Calibration Methods

The purpose for calibration of LFM is to determine how the torsion force relates to the detected voltage [12] [13]. Martin Munz provides a review of available calibration methods for LFM. This section will provide a quick overview of the methods discussed in the review, and then describe the method that would be implemented in the project.

The review presents five different categories for calibration of LFM: direct application of a force off-axis to the long axis of the cantilever, compliance, suspended platform, wedge, and torsion resonance. Of these, only wedge provides both the parameters needed for calibration, while the rest only determine the torsional stiffness of the cantilever [44]. The other methods require a separate method for calibrating the sensitivity of the photodiode. Two problems arise from using the wedge method. First, since the tip will wear and change with use, the calibration constant can also change. Second, the calibration method does not provide a value for the torsional stiffness, but rather provides one calibration constant to account for both parameters. The calibration method in this project falls under the wedge method; however, it addresses the shape change problem by minimizing the wear that occurs during the calibration process.

The general wedge methods work by running the cantilever along a substrate with a known slope at different load forces [45]. The angle of the slope forces the cantilever to twist a certain amount; figure 2.7 shows a simple schematic of the process. This twisting creates a
friction loop, a loop that represents the twisting of the cantilever during a scan image in both the forward and reverse traces (figure 2.7.B). By analysis of the friction loop, it becomes possible to determine a calibration constant that combines the sensitivity of the photodiode and the torsional stiffness of the cantilever. Since multiple images need to be taken at different load forces, this method leads to tip wear. In addition, there is controversy in this process due to the use of a friction model. Some believe that friction is related to surface area; therefore, as the tip wears the calibration constant can change due to increased friction [44]. In addition, the wear will cause the tip height to change, changing the length of the lever arm, and therefore causing a change in the twisting of the cantilever. A method developed by Anderson et al. addresses this problem, while also creating a calibration method that is easy and fast to conduct [46].

![Diagram](image)

Figure 2.7: The figure shows schematics of the classical wedge method (A) [12] and (B) a friction loop associated with an LFM image. The angle, $\theta$, is the angle that the slope is raised from the flat surface. Due to static friction, as the AFM head begins to move, the tip stays in place, causing the twisting (the sloped parts of the loop). Once static friction is overcome, the cantilever no longer twists but stays at that angle. The process is repeated in the reverse direction creating the loop.

The work of Anderson et al. builds off the wedge method. It also uses an observable linear correlation between lateral force and voltage. The method addresses the wear by using pulled-micropipettes instead of a wedge. The classical wedge method uses the load strength as the variable; however, since the pulled-micropipette provides a semicircle, it is possible to use the angle, $\theta$, as a variable. This means that only one scan, at one load, is taken to find a
calibration constant between the forces on the surface and the detected voltage, minimizing the wear on the tip. Figure 2.8 shows the angle of interest as well as the forces acting on the tip during a scan.

![Figure 2.8: A) Shows the three coordinate systems used in the derivation of the calibration technique. B) A schematic depiction of the angle, \( \theta \), the angle between the horizontal and a line tangent to the curve where the tip meets the pulled micro-pipette. C) Is a free body diagram that depict the forces that act on the tip during the scan. The variables of interest are described in the text [46].](image)

Through analysis of all the forces interacting with the cantilever and tip, Anderson et al. were able to develop equation 4:

\[
\overline{F}_{lat} = F_{load} \cos \varphi \tan \theta \left[ 1 + \mu^2 \cos^2 \alpha (1 + \tan \alpha \tan \varphi \sec \theta) \right] \\
+ 2A \left[ \frac{\mu^2 \cos \alpha \tan \theta \sec \theta}{1 - (\mu \cos \alpha \tan \theta)^2} \right],
\]

where \( \overline{F}_{lat} \) is the average lateral force, \( F_{load} \) is the load force the cantilever applies to the surface, \( \varphi \) is the angle of deflection of the cantilever in the normal direction, \( \theta \) is the angle
between the horizontal and the line tangent to the curve in the fast scan direction, \( \mu \) is the coefficient of friction, \( \alpha \) is the angle between the horizontal and the line tangent to the curve in the slow scan direction, and \( A \) is the adhesion force between the substrate and tip. Upon inspection of this equation, two things become apparent. First, is that the equation is dominated by the \( F_{\text{load}} \cos \varphi \tan \theta \) term since \( \mu \) is usually less than one and \( A \) is often small relative to \( F_{\text{load}} \); the bracketed term therefore approaches one. Second is its relation to the experimentally observed linear relationship between lateral force and detected voltage. Equation 5 models the experimental relationship:

\[
\bar{F}_{\text{lat}} = \beta \bar{V}_{\text{lat}} + \gamma,
\]  

(5)

the slope provides the desired calibration constant, \( \beta \), \( \bar{V}_{\text{lat}} \) is the average detected voltage and \( \gamma \) is the y-intercept. Figure 2.9 shows the linear relation between lateral force and detected voltage [46].

![Figure 2.9](image)

**Figure 2.9:** The linear relation between lateral voltage and lateral force. The calibration constant, \( \beta \), is the slope of the line of best fit [46].
Through calibrating the cantilever, quantitative analysis through LFM becomes possible. For most aspects of tribology this provides substantial evidence; however for the study of nanoparticle adhesion, more information is needed. This is because LFM can only provide information on only one particle at a time due to the nature of the machine. To compensate for the lack of data points, we will also use different methods that are able to study the adhesion on a macro level.

2.6 Macroscopic Force Measurements

The literature presents many different methods to determine the force necessary for the removal of a micro-particle, a particle between 0.1 and 100 µm in size, from a surface; however, there seems to be a lack of research directed towards nanoparticle removal. Thankfully, Kumar et al. determined that the adhesion interaction due to van der Waals and electrostatic forces are scalable between a micro- and nano- particle [47]. This means that the principles that govern microparticle adhesion and removal are the similar to that of nanoparticles.

A literature review conducted by Visser discusses mechanisms behind both the adhesion and removal. This paper will discuss two of the removal models presented in the paper that are the most prevalent in research and to this project. These two models are centrifugal removal and induced liquid flow [48].

The centrifugal model presents the only direct measurement of particle adhesion since the only force applied to the particle is centrifugal [48]. For a particle to be removed from a substrate, the centrifugal force, \( F_C \), must be greater than the lateral adhesion force, \( F_A \). Figure 2.10 and equation 6 model how to determine \( F_C \). To find the effective mass of a particle with radius \( R \), the medium density, \( \rho_m \), is subtracted from the particle density, \( \rho_s \), and multiplied by
the volume of the particle. $F_C$ is found by multiplying the mass of the particle by the rotational acceleration, $\alpha$.

Dejesus et al. developed a simple method to quantify the data for this process [49]. First, the centrifuge is placed under a vacuum to minimize the $\rho_m$ term. Second, scanning electron microscope (SEM) images were taken of the surface to determine the number density. The samples were placed into the centrifuge, and spun at different speeds. After each test, SEM images were then taken to determine which force reduced the number density by 50% [49].

Figure 2.10: A force diagram of the centrifugal model for particle removal. The particle will be removed when $F_c$ is greater than the force of adhesion ($F_a$)

$$F_A < F_C = \frac{4}{3} \pi R^3 (\rho_S - \rho_m) \alpha.$$  \hspace{1cm} (6)

When implementing this calculation on the nano-level one major problem is observed. Since the $R^3$ term governs the equations, and since the radius of nanoparticle, by definition, is upwards of three orders of magnitude smaller than microparticles, the centrifuge may not be able to spin fast enough to remove the particle from the surface. The use of a centrifuge for nanoparticle removal may not be appropriate for nanoparticles.
An alternate approach occurs by liquid flow. The induced liquid flow method is the most common method for particle removal found in the literature [50] [51] [52]. This method is popular due to the easy setup, quick experimental process, and real time analysis of the information; however, in contrast to the centrifugal method, where the centrifugal force is well understood, in the flow method, the liquid near the surface might flow more slowly than it does further from the surface [51]. Figure 2.1 shows how the flowing liquid will apply force to the nanoparticle. This is due to the potential for other forms of movement the particle can undergo outside of direct removal. Sari describes how a particle on a surface can also slide or roll during the experiment as well as the desired lift effect [52]. Yiantsios and Karabelas also show that the force necessary to slide or lift a particle is on the same order of magnitude, however the rolling force is much less. Equation 7 presents a simple model for the force applied to the particle:

\[ F = \rho A v^2, \tag{7} \]

where \( F \) is the force on the particle, \( \rho \) is the particle density, \( A \) is the cross-sectional area, and \( v \) is the velocity of the flow.

![Figure 2.1](image.png)

Figure 2.11: Shows how a liquid flowing over the surface would apply a force to the surface. \( V \) is the velocity of the liquid, \( R \) is the radius and \( F \) is the force applied. When \( F \) is larger than the force of adhesion, the particle is removed from the surface.

Both of these methods are reliable and provide useful tools for the determination of the adhesion force. However, as will be discussed later, they are not applicable to work on the nano-
level due to a change in the magnitude of R. A new method to analyzed adhesion on the nano-level is discussed in methodology Section 3.6.
Chapter 3 Methodology

This section maps out the experimental process that establishes a qualitative analysis method for the adhesion of nanoparticles to substrates. It begins with the chemical processes, starting with methods for silver nanoparticles synthesis, leading into functionalization techniques, and ending with the different adhesion mechanisms forming the experimental samples. Following the chemical processes are sections on the physical analysis of the prepared samples. These sections begin with characterization techniques, then the qualitative analysis of the samples through macro-flow techniques. This methodology explains the synthetic processes—the synthesis of silver nanoparticles and functionalization of the substrate—in general terms. The in depth processes are available in Appendices A and B respectively.

3.1 Equipment and Chemicals

Synthesis of silver nanoparticles (Ag NPs) utilizes silver nitrate ($\text{Ag}_2\text{NO}_3$), sodium borohydride ($\text{NaBH}_4$), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), and medium molecular weight polyvinyl alcohol (PVA). The functionalization of the carbon substrate utilizes sulfuric acid ($\text{H}_2\text{SO}_4$), nitric acid ($\text{HNO}_3$), hydrogen peroxide ($\text{H}_2\text{O}_2$), ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$), 1-ethyl-3-(3-dimethylaminopropyl)-cabodiimide (EDC) and N-hydroxysuccinimide (NHS). Worcester Polytechnic Institute chemical stock room provided all chemicals. The carbon substrate is 490HP-AB SPI-3 graphite from Structure Probe Inc. A Veeco AutoProbe M5 model atomic force microscope (AFM) analyzed the Ag NPs adhesion strength on the graphite substrate with a 15 N/m NanoWorld Pointprobe® SEIHR cantilever. Atomic Absorption Spectrometer used to determine the concentration of the samples is a Perkin Elmer AAnalyst 300.
3.2 Synthesis of Silver Nanoparticles

Two methods were used to synthesize the silver nanoparticles. Method 1 was the chemical reduction of AgNO$_3$ using NaBH$_4$ as a reducing agent as described by formula 3.1:

$$Ag^+ + BH_4^- + 3H_2O \rightarrow Ag^0 + B(OH)_3 + 3.5 H_2$$  \hspace{1cm} (3.1)

First, the NaBH$_4$ was brought to 0 °C, followed by the addition of AgNO$_3$ at about one drop per three seconds to the solution. The drop-wise addition continued until a 3:2 ratio between NaBH$_4$ and AgNO$_3$ was achieved. A faster drop rate leads to increased particle size and agglomeration. A color change from clear to light yellow occurs early in the reaction (within 2 mL). If the solution turns grey, bulk silver formed. Continuous stirring for 3 hours at 0° C improves yield. NaBH$_4$ was in excess to act as a capping agent [21]. Appendix A.1 contains the detailed experimental process for the chemical reduction method.

Method 2 synthesized Ag NPs via thermal decomposition of silver oxalate (Ag$_2$C$_2$O$_4$) model by formula 2:

$$2Ag_2C_2O_4 \xrightarrow{\Delta, PVA} 2Ag + 2CO_2$$  \hspace{1cm} (3.2)

First, two units of AgNO$_3$ reacted with one unit of H$_2$C$_2$O$_4$ to form Ag$_2$C$_2$O$_4$. The product was dried overnight at approximately 60°C. Next, a 1:5 weight ratio mixture of Ag$_2$C$_2$O$_4$ to PVA was prepared in a reaction vessel. Attached to the reaction vessel were a reflux condenser and a T-adapter. The reaction vessel was nitrogen purged for 10 minutes, then refluxed for three hours at 100° C. The decomposition to Ag NPs is thermodynamically favored over bulk silver due to the use of PVA [16]. Appendix A.2 contains the detailed experimental process for the chemical decomposition method.
3.3 Functionalization of Carbon Substrate

Functionalization of the graphite substrate was done in two ways. The first added carboxyl groups to the surface. The second added an ethylenediamine ligand (C\textsubscript{2}H\textsubscript{7}N\textsubscript{2}) to the surface.

The first technique functionalized the surface with carboxyl groups, as shown in figure 3.1. To do this concentrated HNO\textsubscript{3} (16 M) and H\textsubscript{2}SO\textsubscript{4} (18.4 M) were mixed in a 1:1 ratio. Next, the acid mixture and graphite substrate were placed into a reaction vessel and refluxed for three hours at 120ºC. Neutralization of the functionalized substrate occurred upon completion. The sample was removed from water bath and dried overnight [20]. Appendix B.1 describes the detailed experimental process for the carboxyl functionalization.

![Figure 3.1: A schematic representation of the functionalization of a carbon substrate through HNO\textsubscript{3}+H\textsubscript{2}SO\textsubscript{4} to form carboxyl groups on the substrate. A represents a native carbon substrate, where B shows the structure of the carboxyl ligand after functionalization.](image)

The second technique functionalized the surface with ethylenediamine ligand, as shown in figure 3.2. The process began with a carboxyl-functionalized substrate. The sample is submerged in a 1:1 mixture of EDC and NHS for five minutes. Next, the sample is immersed in ethylenediamine for ten minutes [31]. Appendix B.2 describes the detailed experimental process for the ethylenediamine ligand functionalization.
Figure 3.2: A schematic representation of the functionalization of a carbon substrate undergoing a substitution reaction from an acid to an ethylenediamine ligand. A represents the prerequisite carboxyl group, where B shows the ethylenediamine ligand.

3.4 Adhesion of Silver Nanoparticles to Carbon Substrate

The experiments produced ten samples for study. These samples varied in functionalization of the carbon substrate, the synthesis techniques of Ag NPs, and the adhesion mechanisms of the NPs onto the carbon substrates.

The first two samples used native graphite as the substrate. Ag NPs from both Chemical Reduction and Thermal Decomposition methods are added drop-wise to separate graphite samples. The samples dried overnight.

The last eight samples involved the functionalized graphite substrates. After substrate functionalization by the aforementioned techniques, Ag NPs were deposited to the substrates by two adhesion mechanisms. First, the NPs from both chemical methods were added drop-wise to the surface. Second, is in situ addition of the NPs, where the Ag NPs are prepared with the substrate in the reaction mixture. The samples dried overnight.
3.5 Transmission Electron Microscopy, and Infrared Spectroscopy

Transmission Electron Microscopy (TEM) and Infrared Spectroscopy (IR) characterized the samples throughout the process to ensure accuracy and proper synthesis. TEM was employed to measure the diameter of the NPs and check for possible agglomeration. IR confirmed the carboxyl and enthlenediamine functional groups on their respective substrates.

3.6 Bulk Removal Technique

Since LFM will only remove a small number of particles at a time, a bulk removal method is needed. This project intends to show a correlation between synthesis techniques and adhesion strengths. For this reason, we measured the decrease of particle concentration at a constant force. To do this the particle density on the nanocomposite (the substrate with adhered nanoparticles) was determined through Atomic Absorption Spectroscopy (AAS).

To begin, nanoparticles were adhered to four identically functionalized substrates. One sample is the control while the others have the nanoparticles removed through physical means. For consistency, both nanocomposites have one side of the substrate removed for reasons that become apparent later. To remove one side of the substrates, the substrate was placed on a sheet of tape. The substrate was then cut away from the tape along the edge where the substrate meets the tape.

The control sample is then treated by 15 mL of 16 M nitric acid. The nitric acid will break down the nanoparticles into silver ions. The silver solution was analyzed by AAS, providing the concentration of silver on one sample. An assumption was made that since both samples are synthesized under identical methods, the concentration of the silver on the surface should be identical.
AAS is a very sensitive technique to measure concentration, able to reach parts per billion, and is a common method for detection of metal in solution. The process uses quantum mechanical properties of atoms to determine concentration; namely, that the energy needed to excite an electron is specific for each element. Figure 3.3 shows a schematic of an AAS. To measure the concentration of a sample, a flame atomizes the sample. A light, with the same energy as the excited state of the sample, is passed through the sample. By comparing these results to a blank, it is possible to determine concentration since the amount of light absorbed is related to the concentration of the sample [53].

![AAS schematic](image.png)

Figure 3.3 A schematic of an atomic absorption spectrometer. The hollow cathode lamp produces a light with the same energy needed to raise an electron of the sample to the excited state. By comparing the results to a blank, it is possible to determine the concentration of a sample with sensitivity of a few parts per billion [53].

To remove particles from the substrate, a single bristle is run along the surface. The force, \( F \), is found by modeling the bristle as a simple spring, as seen in equation 1 and 2:

\[
F_{mag} = kx, \quad (3.3)
\]

\[
k = \frac{3E\pi D^4}{64L^3}, \quad (3.4)
\]
where $x$ is the displacement, $k$ is the spring constant, $E$, is the Young’s modulus, $D$ is the diameter, and $L$ is the length of the bristle. The deflection of the bristle is measured under an optical microscope and kept in the tens of microns range. Figure 3.4 shows the interaction between the bristle and particle. To view the deflection on the microscope, the sample was taped to a vertical surface.

![Diagram](image)

**Figure 3.4:** A diagram of how the bristle interacts with the particle. The amount of deflection is related to the force applied to the particle.

After the test, the sample is prepped under the same conditions as the control. The change in concentration shows that particles are removed at a given force. The sample with the lowest change in particle concentration has the largest strength of adhesion.

### 3.7 Lateral Force Microscopy

The calibration method developed by Anderson et al. at Worcester Polytechnic Institute, which utilized the linear relationship between lateral force and the detected voltage, was implemented as the calibration method for this project [46]. This provides a calibration constant $\beta$ in the equation, $F_{\text{lat}} = \beta V_{\text{lat}} + \gamma$. 
Chapter 4 Results and Discussions

To determine the adhesion of nanoparticles to a substrate, this project synthesized silver nanoparticles, functionalized a variety of substrates, and determined a qualitative method to determine adhesion strength. The determination of a new qualitative bulk removal method was necessary since traditional methods are not applicable on the nano-scale. This section begins with the results of the classification of the nanoparticles and substrates. Next, is a discussion on why the traditional methods are not applicable on the nano-scale, and how this method addresses this problem. Lastly are the results from the bulk removal experiment.

4.1 Nanoparticles

The chemical reduction method, as described in Chapter 3.2 worked as expected. Since this method is rate dependent, adding a buret to the original method standardized the drop rate, leading to more consistent synthesis. Color change, from clear to yellow is observed after 1 mL of AgNO$_3$ is added to the solution. If this does not happen two things could have occurred. First, the solution stayed clear, meaning no reaction occurred. Second, if the solution turned gray, meaning bulk silver began to form. No research was conducted onto what lead to no reaction; however, it is likely due to improper storage of the NaBH$_4$. The formation of bulk silver occurs when the reaction rate is too high, from either too fast drop rate or too high temperature. The introduction of the buret addressed the drop rate problem finding that 1 drop per 3 seconds worked best.

A few problems existed early on with the thermal decomposition method. The synthesis of nanoparticles was inconsistent. During some attempts no reaction occurred, while in others bulk silver formation occurred quickly. It was determined that the cause of the inconsistencies was
due to the equipment used. Originally the setup called for an oil bath. After multiple attempts, it was realized that the oil bath did not maintain a consistent temperature. Once the oil bath was replaced with a heating mantel and thermocouple, this method began to produce reliable nanoparticles.

TEM was used to characterize the size, size distribution, and agglomeration of the silver nanoparticles. Figure 4.1 is the TEM image for both the chemical reduction (A) and thermal decomposition method (B). The images show that the nanoparticles are uniformly distributed over the surface, have little size distribution, and lack agglomeration. The inset shows the average size of the nanoparticles, between 5 to 10 nm.

Figure 4.1: TEM images for both the chemical reduction (A) and thermal decomposition (B) methods of nanoparticle synthesis. Both methods produced products that lack agglomeration and have little size distribution. The insets show the size distribution of the nanoparticle for each method. Both methods produced particles within the 5 to 10 nm range.

4.2 Substrate Functionalization

Once the oxidized substrate was synthesized and confirmed using IR, four samples underwent a substitution reaction, replacing the carboxyl group with an ethylenediamine group.
Figure 4.2 is the IR spectra for both the carboxyl and ethylenediamine functionalized substrates. The 3500-2500 cm\(^{-1}\) stretch in figure 4.2.A provides evidence for a C-O-H group. The broad peak is characteristic of this group due to hydrogen bonding between water molecules. The 1700 cm\(^{-1}\) is characteristic of a C=O stretch. The broad peak again is due to hydrogen bonding. Figure 4.2.B is for the ethylenediamine substrate. The peaks at 3300 and 1500 cm\(^{-1}\) suggest the existence of the ethylenediamine ligand.

![IR spectra](image)

**Figure 4.2:** Shows the IR spectra that confirm the functionalization of the substrates used in this experiment. The peak between 3500 and 2500 cm\(^{-1}\) as well as at 1700 cm\(^{-1}\) in A suggest the existence of the carboxyl group. The 3300 and 1500 cm\(^{-1}\) peaks in B suggest the existence of the ethylenediamine group.

### 4.3 Lateral Force Microscopy

This project implemented lateral force microscopy to estimate the adhesion strength of silver nanoparticles dropped onto a carboxyl functionalized carbon substrate. This estimate determined the base force needed to remove a nanoparticle from a substrate. Figure 4.3 shows AFM and LFM images of the substrate at different set points. Images A and B are at a set point of 0.7 V and images C and D are at 4.1 V. Increasing the set point increased the force applied to the surface, and therefore the nanoparticle. The figure shows that at a set point of 4.1 V nanoparticles are removed from the surface. A relation between set point and force is about 100
nN per V. This means that we can assume that the force needed to remove a particle is about 410 nN and is on the order of 100s of nN. The full range of AFM and LFM images can be found in Appendix C.

Figure 4.3: Shows how an increase in set point, from 0.7 V in A and B to 4.1 V in B and C, resulted in the removal of nanoparticles. Nanoparticles 1 and 2 stay in position as the set point increases, however nanoparticles 3 and 4 are removed. This set point relates to about 410 nN.

4.5 Scaling

During the course of this project, it became apparent that classical methods to determine adhesion strength of microparticles are not applicable on the nano-level. This is due to the change in magnitude of the radius of the particle as it shrinks from the micro to nano. Based on qualitative LFM measurements, it was decided that the adhesion force ranged between 100 and 900. From the estimates it is possible to reverse calculate the speed at which a fluid must pass over the surface to remove a particle. The equations for flow method:
\[ F_a < F_f = \rho (\pi r^2) v^2, \]  
(4.1)

where \( F_a \) is the adhesive force, \( \rho \) is the density of the flow, and \( r \) is the radius of the particle. The governing variable in this equation is the \( r^2 \) term. The technique works on the micro-level with the magnitude of the radius being \( 10^{-6} \); however, a change in the radius to the nano-level, \( 10^{-9} \), produces a magnitude change of three. For example, for a microparticle with an adhesion force of 100 nN, an airflow needs to be 20 m/s, while the same adhesion force on the nano-level requires a flow of 20,323 m/s. A similar problem occurs with the centrifugal method, with the governing variable being the \( r^3 \), as shown in equation 4.2.

\[ F_A < F_C = \frac{4}{3} \pi r^3 (\rho_S - \rho_m) \alpha. \]  
(4.2)

It is possible to offset the small radius problem in the liquid flow method. Since the formula for fluid removal is based on the change of momentum from the fluid to the nanoparticle, atoms in the fluid must encounter the particle. The density of air and water is too low to provide enough force to the sample. By selecting a liquid with a higher density it may be possible to remove the particles though that method; however, by increasing the density of the fluid, one is also increasing the viscosity, and potentially, cost. A fluid with a high viscosity may prevent the fluid from moving at adequate speed.

The bulk removal method developed by this project is able to apply the force needed to remove the particles. From equation 3.4, we were able to determine that the spring constant for the bristle is \( 1.35 \times 10^{-2} \frac{N}{m} \). This means that a deflection of 10 microns would apply 135 nN of force to the surface. Figure 4.4 shows the values we used to determine the spring constant.
### Diameter (cm) Length (cm) Young’s Modulus (N/cm²)

<table>
<thead>
<tr>
<th>Diameter (cm)</th>
<th>Length (cm)</th>
<th>Young’s Modulus (N/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0068</td>
<td>1.0</td>
<td>100000</td>
</tr>
</tbody>
</table>

Figure 4.4: This figure demonstrates the values used to calculate the spring constant of the bristle used in this project.

#### 4.6 Bulk Removal

Our process of bulk removal was successful in removing silver nanoparticles from the substrates. Figure 4.4 shows the remaining concentration of silver—determined by atomic absorption spectroscopy—on the substrate after qualitative forces of high, medium, and low, were applied to the surface. A clear trend of decreasing particle concentration as a function of the force applied is observed for the drop method.

![Drop Method: Remaining Concentration Vs. Qualitative Force](image)

Figure 4.5: A graph of the remaining concentration of silver nanoparticles vs. a qualitative force measurement. The graph shows a clear trend between the force applied and the concentration of nanoparticles on the surface of the substrate.
The results of the in-situ experiments were less conclusive than the drop method. No clear trend is observed when relating the remaining concentration and the qualitative force measurements as shown in figure 4.5 A. By inspecting the in-situ samples under an optical microscope, it was decided that the functionalized substrates have complex morphology. The complex morphology leads to an irregular surface area. Figure 4.5 B demonstrates the complex morphology of the sample. Since the in-situ method synthesized the silver nanoparticles directly onto the substrate, the nanoparticles cover the sample almost completely. This has lead us to believe that the concentration of the nanoparticles in the AAS test is proportional to the surface area of the substrate.

No quantitative data was collected during the course of this project. This is due to inconclusive images gathered from the optical microscope. The difficult arose from two sources. Primarily, it came from lack of control over the deflection of the bristle. Static friction held the bristle tip in place during the experiment. The tip would then snap to normal once the force on the bristle overcame the static friction. This made imaging the deflection just before the “snapping point” difficult
Figure 4.6: The results from the in-situ method show no correlation between the remaining concentration of silver nanoparticles and the qualitative force measurement (A). The inconsistency comes from the complex morphology of the graphite substrate (B).
Chapter 5 Conclusion & Future Work

Our project was successful in both the synthesis of silver nanoparticles and the functionalization of the graphite substrates. TEM confirmed the size and morphology of the nanoparticles to be between 5 and 9 nm for both the chemical reduction and thermal decomposition methods. IR confirmed the functionalization of both oxidative and amine substituted substrates.

We also concluded that the existing techniques used to determine adhesion strength of microparticles are not applicable on the nano-level. This is because the governing variable in these methods is the particle radius. The change in the magnitude of the particle radius form the micro- to the nano- prevents the use of the classical methods. After this realization, the driving motivation of this project was the development of quantitative bulk removal method.

This project has developed and tested a preliminary process to measure the adhesion of nanoparticles to substrates by brushing the particles off the surface. The method proved successful in removing particles from a substrate; however, a few refinements are needed to perform this method quantitatively. First, the static friction between the surface and bristle caused the bristle to snap along the surface, this coupled with moving the bristle along the surface by hand, makes creating reproducible forces difficult. Using a machine to manipulate the bristle should overcome both of these problems. In addition, the use of a video recorder instead of a camera will allow for easier detection of the deflection just before the snapping point. Second, the bristle is only moved in one line along the surface of the substrate. A method that applies force to a larger area, such as multiple bristles, would improve the accuracy of the results. Lastly, this project did not account for the concentration of nanoparticles based on total
surface area of the substrate. The addition of a method to determine the surface area of the substrate is necessary. A Brunauer-Emmett-Teller test—commonly used to determine the surface area of powders—may be applicable for this application.

With this technique, it becomes possible to measure how a nanoparticle will be affected in nature. Conventional methods to study how nanoparticles adhere to a substrate measure forces from the normal direction. These measurements are not able to determine how a nanoparticle will be affected by lateral forces, which they are more likely to encounter in nature. With little manipulation, this method can be applicable to a variety of applications. Any generic substrate, ranging from metal, to ceramics, and even biological, can have nanoparticles applied to it and use this method to remove them.

This project also determined that the speed at which water needs to flow over the substrate is well below the speeds necessary to remove the particle from the substrate. This force, however, is instantaneous, as in one time. To fully understand the life-cycle of the particle, it is important to understand how a constant force overtime affects the adhesion of the nanoparticle. This can be conducted using the classical flow method at the operational flow rate for a given amount of time.

One such method could be to set up a circular water flow, where the flow rate can be set and maintained for a week. After a week the water is collected, and replaced with new DI water. The sample water can then be tested through atomic absorption spectroscopy. This test will provide evidence on how long the nanoparticles will stay on the substrate, and can possibly provide evidence on which surface chemistries provide the longest life spans.
References


Appendices

Appendix A Synthesis of Silver Nanoparticles

Appendix A.1 Chemical Reduction of AgNO₃

1. Prepare two solutions:
   a. 0.0020 M AgNO₃ (aq)
   b. 0.0030 M NaBH₄ (aq)

2. Using a graduated cylinder, pour 30ml of 0.0030 M NaBH₄ in a jacketed beaker with the temperature at 0°C. Allow cooling for at least 20 minutes.

3. Place a stir bar in the jacketed beaker, center the assembly on the stir plate and begin the stirring.

4. Pour 10mL 0.0020 M AgNO₃ in a burette covered with aluminum foil. Add the solution drop-wise at a rate of 0.5 drop/second, until there is none left. After 2 mL has been added, the solution should turn a light transparent yellow. When all (or most) of the AgNO₃ has been added, the solution should be a medium transparent yellow. This should take approximately 5 minutes.

5. **Stir In 0°C Bath For 3 Hours**

6. The product should be transparent yellow once the reaction is completed and should remain yellow, although it may darken somewhat. Record the appearance of the product as soon as stirring is stopped and after waiting for approximately 5 minutes. If the product has aggregated and turned gray---repeat the synthesis due to bulk silver formation.
Appendix A.2 Thermal Decomposition Ag$_2$C$_2$O$_4$

A.2.1 Formation of Ag$_2$C$_2$O$_4$

1. Prepare two solutions:
   
   a. 0.5 M AgNO$_3$ (aq)
   
   b. 0.5 M Oxalic Acid

2. Using a graduated cylinder, pour 50ml of AgNO$_3$ into a beaker.

3. Place a stir bar in the beaker and begin stirring.

4. Using a graduated cylinder pour 30 ml of Oxalic Acid into a beaker.

5. Filter resulting white precipitate and then wash with DI water.

6. Dry at 60º C overnight. Store in an amber bottle and wrap with aluminum foil.

A.2.2 Thermal Decomposition of Ag$_2$C$_2$O$_4$ to form Ag NPs

1. Set up reflux apparatus under a nitrogen blanket, see figure A.1.

Figure A.1: The reaction apparatus for the synthesis of silver nanoparticles through thermal decomposition
A. Heating Mantle or Oil Bath

B. Round Bottom Flask Reaction vessel with stir bar

C. Reflux tube

D. T-joint

E. Nitrogen Flow

2. Add 40ml of DI water to round bottom flask with stir bar.

3. Add 0.25g of solution PVA to the round bottom reaction vessel.
   a. Heat to 80ºC and stir till dissolved
   b. Let cool to prevent loss of H$_2$O

4. Add 0.05g Ag$_2$C$_2$O$_4$ to the reaction vessel.

5. Purge reaction apparatus, with nitrogen for ten minutes.

6. Reflux for 3 hours under a nitrogen blanket at 110-115ºC.

7. The formation of yellow colloid is observed.
Appendix B: Functionalization Methods

Appendix B.1 Carboxyl Addition Method

1. Prepare a 1:1 mixture of 16 M HNO₃ and 18.4M H₂SO₄
   a. Add Nitric Acid to Sulfuric Acid.
   b. Stir slowly in beaker with stir bar.
2. Decant mixture into a 250 mL round bottom reaction vessel.
3. Set up reflux condenser as described in Appendix A.2.2.
4. Place Native Graphite into reaction vessel.
5. Heat reaction vessel to 120 °C and reflux for 3 hours.
   a. Start with plate on high, once plate reaches 100 °C, reduce hot plate dial to 5.
6. Place sample into cool DI water bath to neutralize.
7. Dry over night at room temperature.
Appendix B.2 Ethylenediamine Substitution Method

1. Prepare a Carboxyl functionalized substrate as described in Appendix B.1
2. Immerse the graphite sample into the $\text{H}_2\text{SO}_4\text{+H}_2\text{O}_2$ for 3 min.
3. Wash with DI water.
4. Immerse into 1:1 mixture of EDC and NHS solution for 5 min. (assumed from literature).
5. Removed Graphite from mixture.
6. Immerse in Ethylenediamine for 10 min.
Appendix C  Atomic Force Measurements

This appendix contains the range of atomic force and lateral force images in which nanoparticles were removed from a substrate during this project.

Atomic Force Microscope Images
Figure C.0.1: Shows changes from initial set point of 0.7 V and final set point of 4.5 V. All left side images are topography images and all right side images are lateral force images.
Appendix D National Science Foundation Highlights

Adhesion of Silver Nanoparticles

**Outcome:** Researches at Worcester Polytechnic Institute are trying to understand how nanoparticles, spheres with a radius only 100x larger than the radius of a single atom, adhere to surfaces. This has led to a development of qualitative and quantitative methods to determine the adhesion strength between the nanoparticle and the substrate.

**Impact/Benefits:** Silver nanoparticles have unique anti-bacterial abilities. By attaching the particles to a carbon surface, it is possible to develop a cheap and effective method to purify drinking water. The nanoparticles, however, cannot distinguish between harmful and helpful bacterial. As such, the escape of the particles from the surface can be detrimental to the environment.

**Explanation:** Our methods allow for a set of standards to be determined that can prevent the escape of particles into the environment. The quantitative method uses an Atomic Force Microscope (AFM) to apply a force directly to individual nanoparticles. This method is time consuming but produces precise information on adhesion. The macro-scale qualitative technique follows the same principles as the nano-scale quantitative method. It is faster and requires less expertise to use; however, it does not allow for precise measurements. By combining the two techniques, it is possible to understand how nanoparticles adhere to a substrate.

Robert Cakounes, Michael Judelson
Worcester Polytechnic Institute

This is an AFM image showing the silver nanoparticles, the bright yellow dots, on a surface. The entire image is 1000 times smaller than the thickness of a credit card.
Appendix E NanoWorcester Poster

Adhesion of Silver Nanoparticles

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Abstract

To better understand the life-cycle of a nanoparticle it is important to study how nanoparticles adhere to substrates. Due to the change in order of magnitude between the micro and nano-scale, conventional methods to study particle adhesion are no longer applicable. This project implemented various removal techniques to study the adhesion strength of silver nanoparticles to different substrates. We estimated that the adhesion force ranged between 100 and 900 nN. We are developing a semi-quantitative method to measure the bulk removal of nanoparticles.

Project Design

Chemical Methods

Chemical Reduction

\[ Ag^+ + Br^- \rightarrow AgBr \]

Synthesis of silver nanoparticles by chemical reduction and thermal decomposition are both bottom-up methods which are reactions in which silver salts in solution in the reaction vessel.

Sintering

\[ Ag^+ + Br^- \rightarrow AgBr \]

Thermal Decomposition

\[ 2AgBr \rightarrow Ag_2O + 2CO_2 \]

Two different layers are being examined for improved adhesion. Since bond strength is related to the surface energy of the substrate, the substrate substrate layer should have stronger adhesion forces.

IR and TEM

The infrared spectrum confirms the functional groups on each sample of graphite. The highlight specific peaks which indicate the attachment of the amine ligand on one sample and oxidation of the other sample.

The TEM images above show successful synthesis of AgNPs through both chemical reduction (A) and thermal decomposition (B). Both methods produced AgNPs with an average particle size between 5-10 nm with little distribution.

Lateral Force Microscopy

As the AFM cantilever moves along a surface, a scratching occurs due to forces present on the tip. As the tip moves from position A to B, the scratching laser moves along the photo diode from the green neutral position to the red position. Through calibration, it is possible to determine the force the tip applied to the surface.

All images are of native graphite with nanoparticles added from drop-wise addition. Top images are AFM and bottom are UFM. Left images correspond to a set point of 0.5 nN right images correspond to a set point of 5 nN. Increasing the set point increases the force the tip applies to the surface and the particle. When the force on the surface is above the force of adhesion, a particle is removed from the surface.

Scaling

• Traditional methods of bulk removal are difficult on nano-level
• Nanoparticles radius \( r < 10^{-9} \)
• Due to particle radius, speeds needed to achieve removal of nanoparticles are impossible to reach with the traditional techniques.

Bulk Removal Method

• Smaller is removed across surface
• SEM images taken before and after to compare particle density

Discussion and Future Research

• Future research on the control of different size distribution can affect antimicrobial properties and ability to change carrier.
• Understanding the life-span of silver nanoparticles and adhesion will provide new applications such as wound healing, coatings, and various electronics.

References

Covering the entire spectrum of adhesion from chemical to thermal and mechanical, these methods are dependent on the size and structure of the nanoparticles.

Acknowledgements

This project was supported by a grant from the National Aeronautics and Space Administration. The authors would like to thank Dr. W. Li for the use of the AFM and Dr. N. A. Gunther for assistance with the TEM.
Appendix F Final Poster

Adhesion of Silver Nanoparticles

Abstract
To better understand the life-cycle of a nanoparticle it is important to study how nanoparticles adhere to substrates. Various removal techniques were used to study the adhesion strength of silver nanoparticles to carbon substrates with different surface chemistries. TEM and IR were used to characterize the NPs and substrate respectively. We developed a qualitative method to determine adhesion strength. A brush is run along the surface and the change in nanoparticle concentration is measured using AAS. Refinement of this process is needed to show a correlation between the force of adhesion and the surface chemistry, namely the determination of surface area of the substrate and the precise control over the brush of the brush.

Project Design

Chemical/Reduction (CR)
Ag⁺ + 3e⁻ + 3H⁺ -> Ag + H₂
Thermal Decomposition (TD)
24Ag₂O₂ -> 48Ag + 4O₂ + 2CO₂

Characterization

Synthesis
Synthesis of other nanoparticle by chemical reduction and thermal decomposition are the bottom-up method which are reactions in which silver exists in solution in the reaction vessel.

Microscopic and Macroscopic Removal Techniques

Lateral Force Microscopy

Bulk Removal Technique

Under an optical microscope, a needle is moved across the sample surface. The deflection is related to the force applied to the surface. The sample is then submerged in 1mM HCl. The change in surface concentration is measured with Atomic Absorption Spectrometry (AAS).

Infrared Spectroscopy

Transmission Electron Microscopy

Conclusion

Future Research

References

Acknowledgements