UNIVERSITY OF CALIFORNIA SAN DIEGO

STM Visualization of Ligand Adsorption on Silver Nanoparticles

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by

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The Thesis of Qingyi Zhu is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

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Chapter 2, is coauthored with Yufei Wang and Professor Andrea Tao. The thesis author was the primary author of this chapter.

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ABSTRACT OF THE THESIS

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Being able to apply in many different fields such as physical sciences, agriculture, and medical sciences, nanoparticles become one of the most popular science research materials with a scale of 1 nm to 100 nm. Many new technologies have been used to study the nanoparticles, including the Scanning Tunnelling Microscope (STM), which can image the molecules' surface at the atomic level. Although STM has been widely applied in imaging noble metal surfaces, the molecular-scale resolution is usually hard to achieve when imagining the nanoclusters

synthesized in solution. Here, we use a low-temperature, Ultra-High Vacuum STM to image silver nanoparticles of different sizes deposited on Au-coated Si wafers and examine the orientation and density of the ligands on the silver nanoparticles. Our study provides a molecular scale characterization of ligand-metal interaction.

CHAPTER 1

INTRODUCTION

1.1 Background and overview

The resolution of human eyes can only see two points between 0.2mm [1]. But a physical body will never limit an imaginative brain. So throughout the years, humans have never been giving up on finding the smallest scale of the world. In 1981, a technique called scanning tunneling microscopy (STM) was invented, eventually giving human beings an insight into the atomic world for the first time. It has the advantages of high-resolution imaging on a femtosecond scale, powerful calculation in scanning tunneling spectroscopy (STS), inelastic tunneling spectroscopy (IETS), and the ability to determine single molecule vibration [2]. With these advantages, it beats the other techniques at that time, making scientists interested in it and developing it rapidly since then. Nowadays, it is more and more applied in observing metal and semiconductors' physical and chemical phenomena, such as scanning small-scale molecules like nanoparticles.

As a molecule on a nanometer scale, the silver nanocube (AgNC) is an ideal object for study using atomic scanning machines such as STM. Thanks to its cube shape, it has six flat surfaces and eight edges, all of which are equal. Since its definition and fundamentals were first discovered by scientists in the late 20th century, they have sought to observe what it actually looks like and how ligands lay on its surface. In this study, the AgNC will be observed using STM in order to better understand its characteristics as well as those of its ligands.

In this paper, we are going to synthesize the AgNC on our own, then use STM and other high-resolution topography techniques to characterize the AgNC. Eventually, the orientation and density of states of ligands on AgNC will be discovered by our scanning.

1.2 Principles of STM Techniques

Scanning probe microscopy is not a name of a single technique but represents a family of microscopy that can be used to measure surface topography [3]. Among all the techniques, STM is most commonly used for determining the properties of a single molecule. A small metal tip with a single atom on the top makes direct and real space measurements possible [4]. The basic principle of STM is quantum mechanics. The tunneling current is calculated by.

$$I_T(Z)=I_0(V)e^{-2\kappa z}$$

Where V is the voltage difference across the two surfaces, and the parameters κ and I0(V) are material-dependent constants [2]. The schematic model of the STM is shown in Figure 1. The model consists of a green STM head, a blue tip, and an orange sample. The tip has only one single atom on its bottom, as only one atom can provide the highest resolution. The feedback loop between the STM head and sample helps maintain a tunneling distance between the tip and sample, ensuring the constant current. With the feedback loop, the tip is less likely to crash, resulting in better topography.

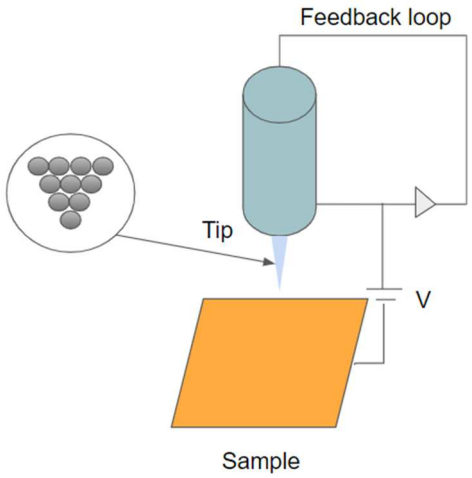

Figure 1: STM schematic.

1.3 Principles of SEM, UV-Vis, and Other Techniques

Scanning electron microscopy (SEM) is another atomic-scale scanning technique besides STM. It can enable images smaller than 15 nm. It typically has a range of 10 to 500,000 times magnification [5]. The basic working function of SEM is transmitting electrons to characterize a single molecule, by accelerating electrons to more than 10 keV [6]. This kind of high-resolution surface topography makes it possible to scan the nanocluster and nanocubes. Also, since it can scan a figure as large as 500 nm in several minutes, which is a much faster and larger image than STM, it is convenient for us to study the whole topography of the molecules.

A useful technique for determining the size of AgNC is UV-Visible spectroscopy. Besides sizes, concentration and aggregation levels can also be determined by it. It has advantages like convenience and easy use, determining the spectra without changing the shape of particles, and fast determination in only several minutes[7]. Since nano-size silver particles interact with visible light as a consequence of the large density of conducting electrons, leading their mean free path larger than their size confinement dimensions. Also, both the real and imaginary parts of the dielectric function in the metal have unique frequency dependence. Together making the reason for surface plasmon resonance existence, which results in the UV-Vis can be used to determine the size and shape of AgNC [8].

Langmuir-Blodgett (LB) technique is able to create highly organized and precisely controlled mono/multilayers, which provide the physical phenomena study at the molecular level. With selective materials, the nonpolar organic solvent can be immiscible with water. By calculating the surface tension, the decomposition of the monolayer can be controlled, making self-assembly possible [9].

1.4 Summary of Contents

STM, SEM, and other techniques have been used to uncover the secrets of the atomic-scale world. To gain a better understanding of these techniques, AgNC was synthesized and used as an object of observation. SEM was utilized to scan the shape and size of the particle itself. In contrast, STM can provide even more detailed information by scanning the ligands on the particles and making them visible to the human eye.

CHAPTER 2

SYNTHESIS OF SILVER NANOPARTICLES

2.1 Introduction

The base of chemistry is synthesized, and all chemistry experiments start with synthesized molecules. Understanding how to synthesize is essential during the analysis of molecules since it will let us more familiar with the chemical and physical properties of the molecule. Nanotechnology is an influencing field in many parts of modern society, such as environmental health, mechanics, optics, and biomedical sciences [10]. Especially, the chemical properties may vary by their sizes. In this paper, we will use silver nanoparticles as the research object, and analyze their properties under 20 nm.

2.2 Methods

To assemble the silver nanocube, a solvent pentanediol needs to be prepared. The synthesis method is based on the Andrea Tao.[11]. The first step starts with placing about 5 ml 0.043M copper (II) chloride ($CuCl_2$) into the pentanediol. For the next step, which is ligand preparation, about 0.20g polyvinylpyrrolidone (PVP) was put into 10 ml pentanediol. Sonicate and vortex both solutions about 2 to 3 times. The third step is preparing the silver solution. Measuring 0.20g silver nitrate ($AgNO_3$) into 5 mL 0.0235M pentanediol and 44μL of 0.043M $CuCl_2$ /pentanediol solution. The whole silver solution should be roughly sonicated for more than

1.5 hours. Sonicate and vertex 9 times for 10 minutes each until all the solvents are fully dissolved. Set the hot plate with heating oil to 168 degrees Celsius for the next step. The final step is to set up the oil bath at 195 C, then inject 500μL of $AgNO_3$ solution every 1 minute. Meanwhile, 320μL PVP injects exactly after 10 seconds of injecting $AgNO_3$ every 30 seconds. Repeat the whole procedure 4 to 7 times to finish the synthesis [11]. To make the AgNC more closed-pack, we used LB to make it self-assemble.

2.3 Results and Discussion

The SEM figure of AgNC is shown in Fig. 2. For large-distance AgNC almost all the silver is shown in a regular cube shape and is of the same size, shown in Fig 2a. Although some defects exist, most of the close-packed samples show the sample results, which are in Fig. 2b. In order to prevent water and other organic compounds from polluting the STM, annealing is essential before placing it in the chamber. Since the scanning conditions require an ultra-high vacuum and liquid nitrogen temperature, we do not want any pollutants to influence the result of the topography. To solve this problem, we anneal the samples three times each time for 15 minutes, which temperatures are 100°C, 130°C, and 150°C, respectively. After annealing the samples, we found that annealing did not cause any significant changes to the AgNC shape, as shown in Fig 2c and d below. Fig 2c is the SEM image of the sample before annealing, and Fig 2d is the SEM image of the sample after annealing. This concludes that annealing at temperatures above 100°C can effectively remove water without affecting the scanning results of AgNC samples.

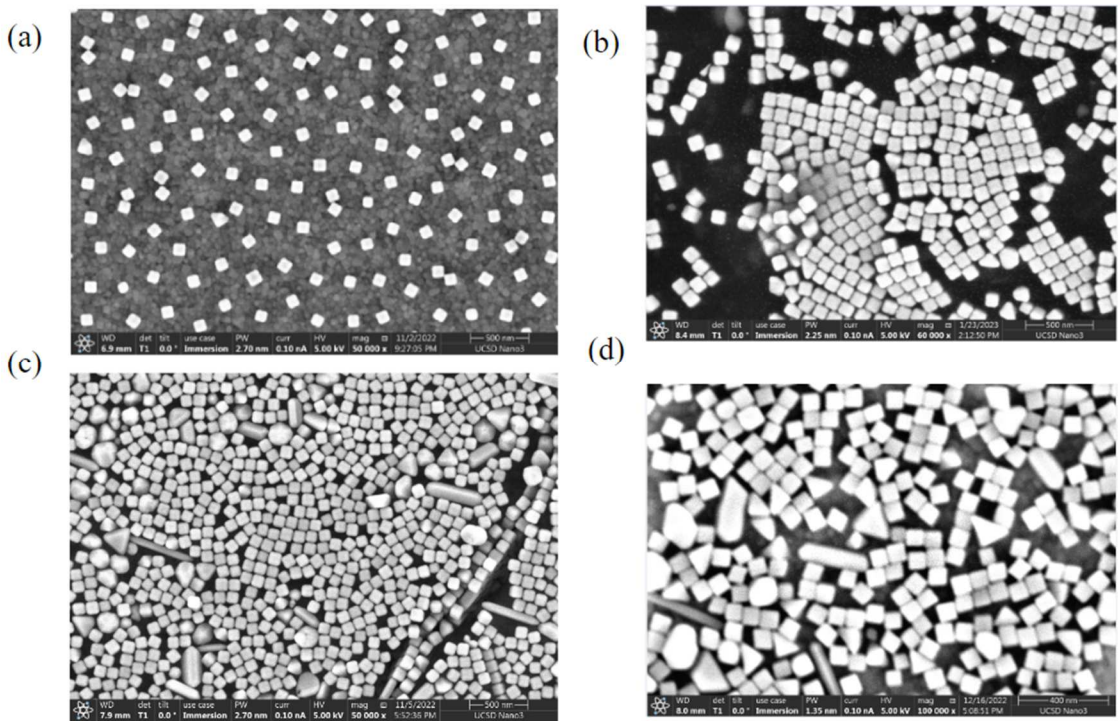

Figure 2: SEM images of AgNC. (a) AgNC samples at a large distance. (b) AgNC sample in a closed pack. (c) AgNC closed-pack sample before annealing. (d) AgNC samples after annealing three times at temperatures 100°C, 130°C, and 150°C, respectively.

2.4 Conclusions

There is no doubt that the assembly of AgNCs was successful, as evidenced by their regular cube shape in both large-distance and close-packed samples. Additionally, even after annealing at temperatures up to 150°C, the samples remained unchanged. Consequently, it can be concluded that annealing at temperatures between 100°C and 150°C is an effective way to remove water and pollutes without compromising the scanning results of AgNC samples.

CHAPTER 3

CHARACTERIZATION OF MOLECULAR LIGANDS ON NANOSTRUCTURES

3.1 Introduction

To prepare for scanning the AgNC sample, we must know if the STM can see the ligands on it individually. To investigate STM potential, we employed 2,6-dimesitylphenyl (DMP) isocyanides[12], one of the ligands commonly used in nanoparticle synthesis, as the study subject for our STM scanning. This allowed us to obtain high-resolution images of the surface and study the binding properties of DMP at the atomic scale.

3.2 Methods

Directly dosing DMP molecules into the STM chamber could be risky since we have no data on its vapor pressure, and it may pollute the chamber. To assess the vapor pressure of DMP, we tested it with an evaporator outside the chamber and found that the vapor pressure is very low, indicating that it is safe to dose it into STM. With this evidence, we proceeded to dose DMP into STM with the Au (111) substrate. The next step involved preparing DMP isocyanide powders in a small crucible and placing it in the evaporator. The evaporator was then heated slowly to vaporize the DMP, while ensuring that the pressure did not exceed 10-9 Torr throughout the process. The valve was opened several times, with each time for 15s, to ensure that the entire surface was immersed. Finally, a tungsten tip was used to scan the gold surface, as the result is shown in Figure 3.

3.3 Result and discussion

Fig 3a shows the bare Au (111) surface, while Fig. 3b shows the Au(111) surface with DMP at a temperature of 77 K. Upon comparing the two figures, some light spots can be seen on the surface in Fig. 3b. By measuring their size and comparing them with the DMP structure shown in Fig. 3c, it was determined that these spots correspond to DMP molecules. The topography of a single DMP molecule is shown in Figure 3d, with a scale bar of 1.75 nm. Based

on these observations, it was concluded that DMP molecules tend to prefer staying on the step edge, followed by the herringbone, while their least favored location is on other flat surfaces.

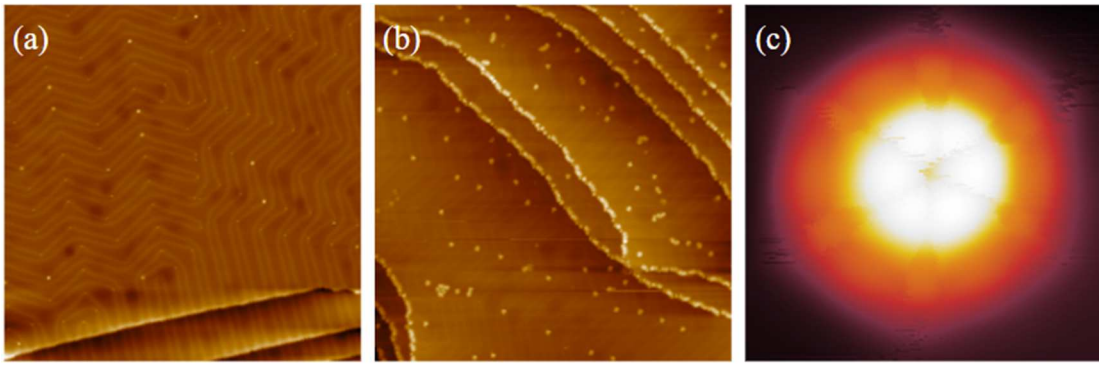

Figure 3: STM image of DMP ligands. (a) Bare Au(111) surface at 77k temperature. Size: 100x100nm. (b) Au(111) surface with dosing DMP isocyanides at 77k temperature. Size: 100x100nm. (c) Single DMP molecule under temperature at 5k. Size: 1.75X1.75nm

3.4 Conclusion

Figure 3 shows that our STM can scan at the atomic level, which is on a nanometer scale. By scanning the sample at a temperature of 77K, we were able to observe the structure of a single molecule. Furthermore, the finding suggests that DMP has a preference for staying on ordered step edges, herringbones, and flat surfaces. Based on this evidence, we concluded that DMP can serve as a stable ligand that binds to the edges of nanoparticles. Moreover, the results further tell that ligands like DMP is tending to bind at the edge of metal to make the metal cube shape possible.

CHAPTER 4

CHARACTERIZATION OF NANOSTRUCTURES WITH SCANNING PROBE MICROSCOPY

4.1 Introduction

SEM is a high-resolution imaging technique that can be used to visualize the surface structure of AgNCs. It alone is not sufficient to observe the finer details of the ligands.

Therefore, we have decided to use STM to analyze the AgNC further. As a powerful technique that can provide atomic-scale resolution by scanning the surface with a probe tip, it can scan at a scale of up to 0.1 nm, which is much smaller than the resolution of SEM. With STM, we can observe the finer details of the AgNCs, including the size, shape, and orientation of the individual ligands on the surface. This will allow us to better understand the chemical and physical properties of the AgNCs and their potential applications in various fields.

4.2 Methods

With all the previous steps completed, it is now time to scan the AgNC with STM. We aim to observe the ligands on the AgNC to determine its density of states and orientation. Initially, we attempted to use larger distance samples for the STM scanning. However, the significant distance made it easy to crash the tip and the rapidly changing tunneling point made it difficult to obtain a clear image. Therefore, we opted to use the closed-pack samples to prevent the tip from crashing and stabilize the tunneling point. This time, we were able to obtain better results.

4.3 Results and Discussion

The STM image of DMP ligands is shown below. Since the AgNC is on a large scale, the scanning rate has to be very slow. Fig. 4a was scanned with a scanning time set from 70 to 90 minutes and a scanning scale of 700*700 nm. As can be seen in the figure, multiple layers of the ligands are visible. To obtain a clearer image and investigate more details of the AgNC, the scanning scale was reduced to 300*300 nm, provide a higher level details that results in Fig. 4b.

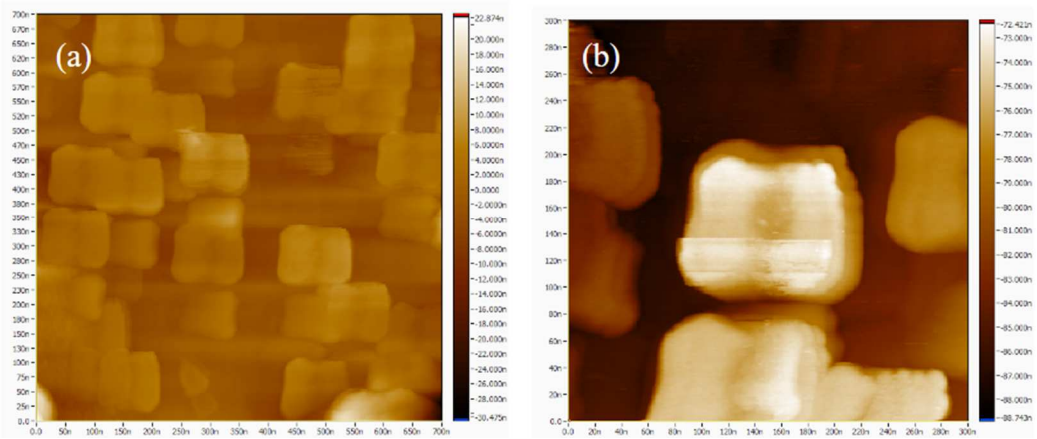

Figure 4: STM image of AgNC. (a) AgNC sample STM images at 77k. Scale bar: 700*700 nm. (b) Single AgNC STM images at 77k. Scale bar: 300*300nm.

4.4 Conclusion

The topography of AgNC demonstrates the remarkable ability of STM scanning on a large scale. Despite the multilayer nature of the sample, STM can determine its height and scan the entire figure clearly. The high resolution of STM imaging allows for precise analysis of the sample, including the detection of subtle changes in its topography. Moreover, STM can be used to investigate the electronic properties of AgNC, providing valuable insights into the behavior of the material at the atomic level. Overall, the results suggest that STM is a powerful tool for studying complex multilayer structures and their electronic properties.

CHAPTER 5

CONCLUSION AND FUTURE PROSPECTS

5.1 Summary and discussion

In this experiment, we synthesized silver nanoparticles with ligands. To visualize their characteristics, we used STM to scan both the nanoparticles and their ligands. Combining the STM and SEM images, we observed that the nanoparticles were cube shaped. The STM scans of

the ligands not only guaranteed the high-resolution ability of STM but also provided evidence that the ligands tended to bind to the edges of the nanoparticles. With this information, we propose a hypothesis that it was because some ligands are tending to bind on the edge of the surface, it is possible the cube shape is contributed by these ligands.

5.2 Future Direction

Despite the progress we have made, there is still a long way to go in our research. As of now, we have not yet discovered the orientation and density of state of the ligands, and the topography of the ligands on AgNC remains elusive. To address this, our next step is to synthesize AgNC with a size of less than 20 nm and scan it using STM.

As previously discussed in chapter 1, SPM has been used to observe the surface of AgNC. However, we have opted for the use of STM for this particular task due to its ability to accurately characterize the molecular ligands. It is important to note that the length of the nanocubes should be less than 20 nm for effective characterization of the ligands. We arrived at this number through the calculation of particles in a three-dimensional box [13] using the Schrodinger equation.

Another important question that remains to be answered is determining the relationship between the shape of nanoparticles and the ligands that bind to them. Given our existing knowledge of the characteristics of DMP ligands, it is essential to further investigate other ligands that also preferentially bind at the edges of nanoparticles. This will help us identify any commonalities between these ligands and their binding patterns. Therefore, the next step in our research is to conduct further scans of the AgNC with a variety of different ligands. Through this process, we aim to establish a clearer understanding of the relationship between ligands and nanoparticle shape.

5.3 Acknowledgements

I would like to acknowledge Professor Shaowei Li for his support as the chair of my committee. Thanks for his support and teaching.

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