

A Thesis Presented to
The Faculty of Alfred University

Pillaring and Intercalation of Gold Nanoparticles in Layered Manganese Oxide

by
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HONORS FOREWORD

As I am in the last stages of completing this document, I have become much more reflective than I thought I would be, and hit with the fact that this is it – the culmination of my time here at Alfred University as a Materials Science and Engineering major. I am glad that I gave myself enough time to complete my thesis and reflect on it as I do so. I am not pressed against the deadline, which has allowed me to really appreciate what I have accomplished. It has been very rewarding to see everything come together and to finally consolidate this large project into a finished product. This document represents not only the year of hard work that I have officially spent on it, but the entire four years of my undergraduate. I feel as though I really have been working on this project for my entire career as a student here at Alfred University. Gaining knowledge, hands-on skill, communication experience, and much more has all prepared me for this undertaking. So to be in this moment, the pinnacle of my undergraduate achievement, it is incredibly gratifying and surreal. I feel like I have not only gained a huge amount of knowledge and experience, but have considerably grown as a person from who I was when I first came to Alfred University only 4 years ago.

In my junior and senior year of high school, as things started to wind down and the time came to decide where to go to college, I still had no idea what I wanted to do with my life. It was a stressful time, and I had a lot of ideas and suggestions, but nothing really felt right. I knew that I liked science, especially chemistry, but didn't know what program or

career in this area would be something I could see myself doing for the rest of my life. I considered the medical field, the pharmaceutical industry, I shadowed a chemical engineer, but nothing seemed to click. Then I learned about Alfred University's various materials engineering programs. It seemed like the perfect fit for me – application of chemistry on an atomic level, while also being able to create and improve real, interesting materials. I was drawn to it because it seemed very unique, but also big-picture – every product, service, and advancement in this world has materials science at its core. I originally came to Alfred University as a Glass Engineering Science major because of the uniqueness of the program, and I was really interested in glass as a material. As I progressed through the curriculum, though, I discovered that I had a broader interest in all types of materials, so around my sophomore year I switched to the more general Materials Science and Engineering program, and have been really happy with that decision. Through these past few years, I've taken many great and informative classes that have given me a wide perspective on materials and presented me many opportunities to explore where my deeper interests lie.

One of those opportunities came the summer of 2021, when I had the privilege of working with Dr. Misture as a research assistant. Dr. Misture's research group deals mainly with advanced ceramic materials, and it was during this summer research position that I discovered an interest in layered ceramic materials. Layered ceramics are materials that have a layered structure at the atomic level. Sheets of strongly bonded atoms are stacked on top of each other, with typically weaker bonds between the sheets. Not only

are they simply fascinating materials, but they have potential for application in electrical systems and energy storage solutions, which are integral to solving the energy crisis, perhaps the most important problem faced today. To contribute to and be a part of something like that, even a tiny, miniscule part, is very exciting and rewarding for me. This discovered interest in layered ceramics is how I ended up settling on my thesis topic.

My thesis involves taking a layered manganese oxide (MnO_2) material, and performing two experiments on it to see if the structure of the material could be changed in a way that may potentially improve its properties. My thesis focuses on whether generating these structural changes can actually work, so measuring the properties of the resulting structures is left to future research. The first experiment was to try and expand the interlayer of the material, which is the space in between the stacked sheets, without causing the sheets to completely separate. If successful, this could increase the surface area of the material, which is very beneficial to energy storage applications. The second experiment was to try and fully separate the layers of the material to get tiny nanosheets, and then restack those nanosheets with gold nanoparticles in between them. This could potentially expand the interlayer, which may be very beneficial as stated above, but gold also has some interesting properties when exposed to light. These properties could be useful for energy applications involving light, such as solar cells.

I realize that not everyone has had the privilege of studying materials science for 4 years, so now I'd like to go through some basic background knowledge to give everyone a better understanding of what was done in this project.

Ceramics cannot be discussed in any scientific or research-focused way without talking about crystal structure. Crystal structure is the long-range, periodic arrangement of atoms in a material. Most solid materials have a crystal structure, with the exception of amorphous materials, like glass. Because of all the different atoms and their possible arrangements, there are many different crystal structures. These different crystal structures can produce different properties, even between materials with the same elements. All crystals, though, can be broken down into one base unit that is repeated throughout the material, called the unit cell. There are different shapes that these unit cells can take, but a simple cubic unit cell is shown below in Figure i.

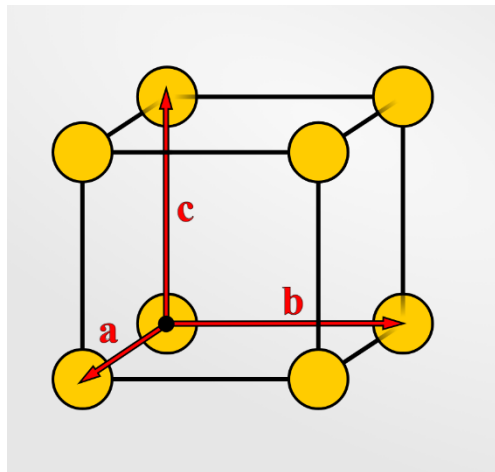


Figure i: Schematic of a simple cubic unit cell.

The direction in the unit cell is represented by the letters a, b, and c. Direction a is in and out of the page, b is left and right on the page, and c is up and down on the page. From this unit cell, it can be seen that there are planes of atoms. Imagine the front face of the cube – that is a plane, and the atoms on the corners of that face are atoms in that plane. Since it is the front face, that plane is denoted as the (100) plane, because to get to that face from the back left corner, you go one unit in the a-direction, and zero in the b and c directions ($a=1$ $b=0$ $c=0$). Something similar can be said for the right and top faces of the cube, written as (010) and (001), respectively. There are many other planes just in this cube using combinations of the abc directions. My material is much more complicated, but I think this helps give a general understanding of atomic planes and their notation. It can be seen that if these unit cells are stacked or placed side by side as shown below in Figure ii, the cube faces come together and form huge planes of atoms.

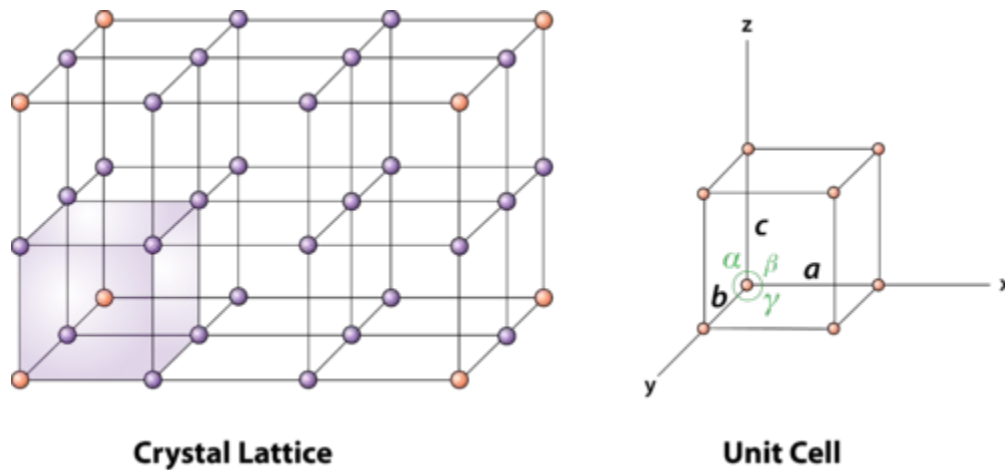


Figure ii: Schematic of how unit cells combine to form a lattice.

Depending on the material and its unit cell, the atom locations and planes will be different. The question then becomes, how do you know what crystal arrangement you have? The answer to that question is X-ray diffraction (XRD). XRD is a characterization tool that allows you to probe the arrangement of atoms in a material. In XRD, a beam of X-rays is fired at your sample at a certain angle. If the angle is just right, the X-rays in the beam will add together after hitting the atoms in the material, giving you a big peak of intensity when detecting the X-rays coming off the material. By figuring out the angle at which this intensity occurs, a lot of information can be acquired about the atomic planes/arrangement of the material. This was the main characterization tool I used in my thesis.

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ABSTRACT

Layered manganese oxide, MnO_2 , was investigated to determine potential ways to produce superior electrochemical properties for supercapacitors and other energy related applications. First, the layered material $\text{K}_{0.45}\text{MnO}_2$ was synthesized and ion exchanged to produce $\text{H}_{0.45}\text{MnO}_2$. This material was then used in two ways. First, an attempt was made to pillar the material using a linear amine and a tertiary amine. Through the use of the Tyndall effect and XRD, the results of this attempt showed that pillaring was unsuccessful, and that the material appeared to exfoliate instead. Second, the material was intentionally exfoliated with TBAOH to produce MnO_2 nanosheets, and then those nanosheets were mixed with gold nanoparticles and flocculated to obtain a layered MnO_2 material with gold nanoparticles dispersed in the interlayer. XRD and SEM images suggest that a disordered, layered material with gold particles intercalated into the interlayer was obtained, with an estimated stacking-direction crystallite size of $104\text{\AA}$. However, the gold did not seem well dispersed, as there were layered MnO_2 sections with no gold found during SEM/EDS analysis. Additionally, floccules that did have gold contained gold particles with an estimated average diameter of $259\text{nm} \pm 137\text{nm}$, which is between 25 and 80 times larger than the nanoparticles initially used. This suggests that the gold agglomerated, and did not evenly disperse as expected.

I. INTRODUCTION

A. Energy Storage

Finding solutions to the current energy crisis is one of the most important tasks faced today. This not only involves developing ways to produce more energy, but also ways to store the energy already produced more efficiently. There is a constant need for devices that can store more energy in a smaller amount of space. Currently, the job of energy storage mostly falls to batteries because they can store a lot of energy for the amount of space they take up¹ (called energy density), but certain drawbacks such as cycle limits, which are the number of times the battery can be charged and discharged before becoming unusable, and the relatively slow speed that they can deliver charge¹ warrant a search for alternatives. Much research has been done on capacitors and supercapacitors to potentially fill this role as an alternative energy storage device.

As opposed to batteries, which use stored chemical potential from an electrolyte solution to drive current, capacitors store their energy in the form of an electric field that forms when two conductive plates separated by an insulator are connected in a circuit¹.

Negative charge builds up on one plate and positive charge on the other, which creates an electric potential between them. The greater the capacitance, or the amount of charge that can be stored on the plates, the greater the electric potential, and the more energy that can be stored in the capacitor, according to Equation 1:

$$E = \frac{1}{2}CV^2 \quad (1)$$

where E is the energy stored, C is the capacitance, and V is the applied voltage. The capacitance of a two parallel plate setup is given by Equation 2:

$$C = \frac{k\epsilon_o A}{d} \quad (2)$$

where C is the capacitance, k is the dielectric constant of the insulating material, ϵ_o is the permittivity of free space, A is the surface area of the plates, and d is the separation distance of the plates. From this equation, it can be seen that there are three ways to increase the capacitance of a two-plate capacitor: increasing the area of the plates, decreasing the distance between the plates, and making the material in between the plates (called a dielectric) a better insulator¹. Decreasing the distance between the plates can only work up to a point, because once the plates get too close there can be a flow of charge, which prevents the capacitor from storing that charge. A lot of research has been done to find better dielectric materials, and currently one of the best materials (in scientific terms, not practical terms) is calcium copper titanate². However, high-performance materials like calcium copper titanate can be difficult to make commercially viable. The final way to increase capacitance is to increase the surface area of the conductive plates, which can be difficult to do with the metal plates typically used.

Supercapacitors, also known as pseudocapacitors, work differently than traditional capacitors, but follow the same basic principles. They can achieve higher power density than batteries and higher energy density than regular capacitors³, and therefore are of

great interest in energy storage applications. In a supercapacitor, two electrodes that have a porous, high surface area material on them are placed in an electrolyte solution with a barrier separating them. When a potential is applied, ions from the electrolyte form a bilayer structure at the electrode-electrolyte interfaces³. Positive ions adsorb to the porous material on the negative electrode, and negative ions on the positive electrode, which creates a potential difference at the surface of each electrode with the oppositely charged ions still in the electrolyte solution. This is what stores the charge in a supercapacitor, and is similar to the positively/negatively charged plates storing charge in a traditional capacitor, but on a much smaller scale. This mechanism is very different than that in a battery, even though an electrolyte solution is used. The advantages of this supercapacitor setup are that first, each electrode acts as its own capacitor, so the electrode pairs effectively create double capacitors. Second, the distance between positive and negative ions in the interface bilayer is very small, on the order of nanometers³, which increases the capacitance of the supercapacitor. Third, the porous electrode material can achieve much higher surface area than a metal plate for the same projected area, which also increases the capacitance. Lastly, supercapacitors retain all of the benefits that traditional capacitors have over batteries, including extremely high cycle life and the ability to release their energy very quickly.

Because the number of ions able to adsorb to the porous material determines the amount of charge that can be stored, if the surface area of this material can be increased, the energy density of the supercapacitor can be increased⁴. Increasing the surface area of this

material can be easier and take up less space than increasing the surface area of the conductive plates of a traditional capacitor. It is therefore extremely important and useful for the practical application of supercapacitors to develop suitable high surface area electrode materials.

B. Layered Materials

Layered materials are very interesting candidates for supercapacitor electrodes, as their natural structure and ability to intercalate, or insert things like ions and molecules in between their layers, give them large theoretical surface area and more active sites for adsorption⁴. Adsorption is the adhesion of molecules or ions to a surface, and is the primary mechanism that controls the electrochemical processes and properties of a supercapacitor⁴. Separating the layers of these materials into 2D nanosheets for similar and other applications is an interesting area of study, and significant work has been done on this topic. Zhao et al. observed improved performance of Sn-based anodes using graphene nanosheets as a buffer in lithium-ion batteries⁵, MoS₂ nanosheets have been investigated for photocatalytic CO₂ reduction⁶, and there are many more application possibilities where surface area plays a key role.

Layered materials themselves, however, may offer unique and useful properties without separating and directly using the nanosheets. If the interlayer spacing of these materials could be increased, or if certain particles/atoms are introduced into this interlayer spacing, the properties of these layered materials could be extremely useful, and may

offer the high surface area and adsorption potential for excellent supercapacitor energy storage solutions.

One possible way to increase surface area, and therefore capacitance, would be to increase the interlayer spacing of a layered material, so that external ions can fit into and reach the inner surfaces of the material. The more ions that can fit into and adsorb to these inner surfaces, the higher the amount of energy the supercapacitor can store⁷. The process of increasing the interlayer spacing of a layered material is known as pillaring, and is done by introducing a specific molecule that wedges its way in between the layers, forcing them further apart. If the incorrect molecule or method is used to facilitate this pillaring, however, it may lead to the sheets completely separating in a process known as exfoliation, which is how 2D nanosheets are formed. When trying to pillar a material, though, this is undesirable. Geng et al. showed that stable pillared materials are achievable, in an investigation of this swelling/exfoliation mechanism in protonated titanates⁸.

Pillaring can be difficult when using processes and materials that readily exfoliate, as there is a fine line between expanding the interlayer a significant amount and separating the layers. Certain materials can also have more difficulty intercalating atoms and molecules into the interlayer. To determine the potential of layered materials that readily exfoliate into nanosheets, as well as the effect of certain molecules that may be difficult to intercalate, exfoliated nanosheets can be restacked back into a layered material, in a

process known as flocculation. Different species can be added just before this flocculation, allowing atoms or molecules to be incorporated into the interlayer as the sheets restack⁹. This process is particularly useful for materials such as MnO_2 , which has difficulty intercalating bulky ions and molecules traditionally, due to a higher charge density in the interlayer compared to other layered materials⁹. The exfoliation/flocculation process is illustrated in Figure 1, adapted from Wang et al.¹⁰ to the materials used in this investigation.

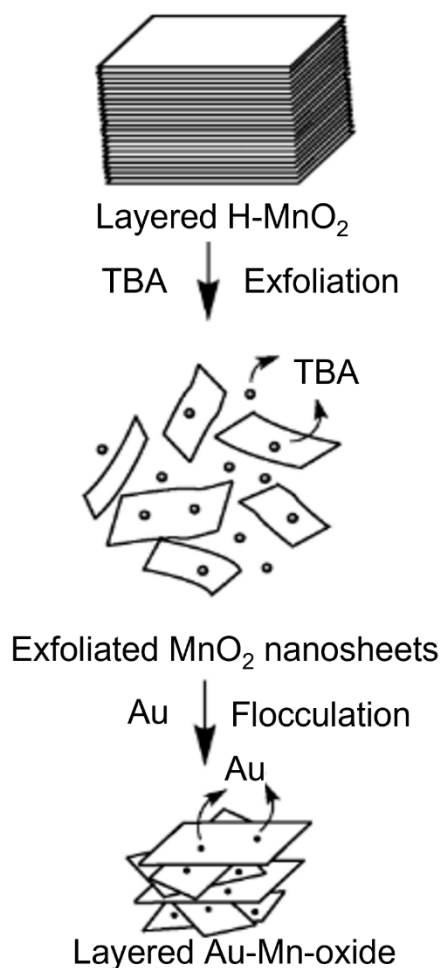


Figure 1: Illustration of exfoliation and flocculation¹⁰.

Layered MnO_2 has its layers forced apart by a large organic molecule called tetrabutylammonium hydroxide (TBAOH). The resulting nanosheets are gathered, mixed with gold particles, and restacked. This results in a layered material with gold particles in the interlayer.

Besides being able to put atoms more easily into the interlayer of certain materials, flocculation also has the potential to increase the interlayer spacing of the material when whatever species was introduced is restacked with the nanosheets⁹. So the pillaring effect can be achieved, even if the material is prone to exfoliation. Wang et. al. used this synthesis method to make a layered manganese oxide material with lithium intercalated in the interlayer, and found that it had a smooth charge/discharge feature from electrochemical tests, showing potential as a cathode material¹⁰. It has also been shown that ion intercalation may increase practical capacity of manganese oxide cathodes¹¹, and that preintercalation of atoms can reduce manganese oxide cathode issues¹². These studies focus on MnO_2 as an electrode material in batteries, but the improvements achieved in them are applicable and useful in supercapacitor applications as well, including structure stabilization, activating more active sites, and promoting diffusion kinetics^{11, 12}. All of this supports that species intercalation, especially in manganese oxide layered materials, may significantly enhance its electrochemical properties, and make it a more suitable supercapacitor electrode material. The potential for pillaring, which could increase the active surface area and adsorption of ions, and therefore energy storage

capacity, also makes these materials exciting and probable candidates for supercapacitor applications.

This knowledge has led to the development of two hypotheses. First, introducing layered manganese oxide to separate solutions of 4-amino-1-butanol (linear amine) and 1-propanol, 3-(dimethylamino)- (tertiary amine), will produce an increase in the interlayer spacing as protons in the interlayer are replaced with these larger organic molecules (i.e. pillaring will occur). Second, exfoliating layered manganese oxide and flocculating it with gold (Au) nanoparticles will cause the nanoparticles to become evenly intercalated in the manganese oxide interlayer as the sheets restack.

The starting material for this investigation is $\text{K}_{0.45}\text{MnO}_2$, which forms sheets of MnO_2 with potassium (K) ions in the interlayer as shown in Figure 2. To attempt pillaring and intercalation of Au particles, K ions must first be swapped with hydrogen (H) ions to form $\text{H}_{0.45}\text{MnO}_2$.

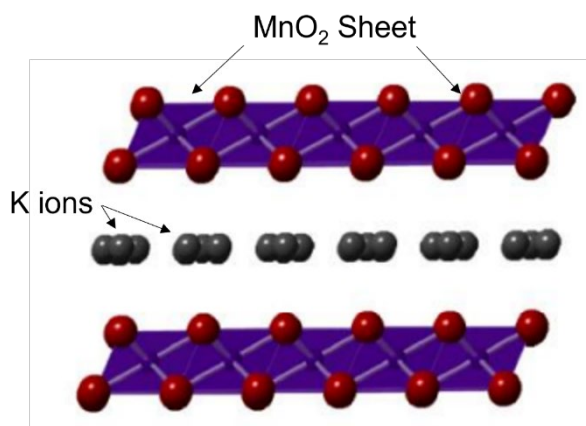


Figure 2: Crystal structure of $\text{K}_{0.45}\text{MnO}_2$, adapted from Metz¹³.

Pillaring was attempted with 4-amino-1-butanol (linear amine) and 1-propanol, 3-(dimethylamino)- (tertiary amine), and exfoliation done with tetrabutylammonium hydroxide (TBAOH). These organic molecules are shown to scale in Figure 3.

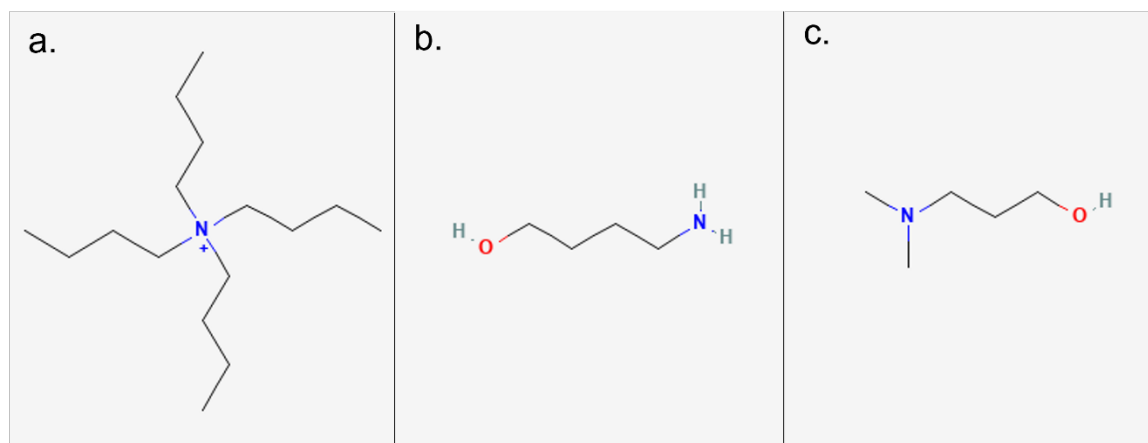


Figure 3: Schematics of a) a molecule of TBAOH, b) a molecule of the linear amine, c) a molecule of the tertiary amine, from PubChem¹⁴⁻¹⁶.

TBA is much bigger, a reason why it is used for exfoliation – it forces the layers so far apart they separate. Amines are smaller, so the expectation is that they won't force the sheets apart as much, and only expand them. TBA is frequently used for exfoliation, and useful for the exfoliation/flocculation aspect of this investigation.

Gold is interesting as an interlayer material for two reasons. First, it may increase the interlayer spacing of the material, which as previously stated can lead to increased surface area and number of active sites. Second, metals can have interesting properties when exposed to light, such as plasmon resonance. Plasmons are collective oscillations of

free electrons in metals¹⁷ that can be excited by electromagnetic radiation. This excitation, however, can only occur at metal surfaces, not the bulk. If small enough gold particles are used, then, to where there is almost no bulk, certain electromagnetic radiation could excite the plasmons into resonance, producing harmonic oscillators that could behave as “nanoantennae”¹⁷. Another very important effect of this plasmon resonance is that “the electromagnetic field near the particle surface is greatly enhanced,” which, “overcomes the resolution limit of ordinary far-field optics, allowing light localization on nanometric or subnanometric scale.”¹⁷ These properties may be very useful for photocatalytic and electrical systems.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Layered Parent Phase $K_x\text{MnO}_2$

The parent phase $K_{0.45}\text{MnO}_2$ was first synthesized. 5.7475g MnCO_3 and 1.5548g K_2CO_3 were measured out and wet milled with isopropyl alcohol (IPA) in an attrition mill for 10 minutes. The resulting slurry was then dried in a metal pan on a hotplate. The dried powder was collected, placed in a crucible, and sintered at 900°C for 12 hours, with a heating and cooling rate of 5°C per minute. X-ray diffraction (XRD) was used to verify the phase. The parent phase was then ion exchanged to obtain $\text{H}_{0.45}\text{MnO}_2$

B. Preparation of Protonated Layered Phase $\text{H}_{0.45}\text{MnO}_2$

0.5g of the parent phase was placed in each of 6 centrifuge tubes with 45mL of 1M HCl. These tubes were then placed in a 40kHz ultrasonic bath for 4 hours and were shaken every 20 minutes to keep the powder from settling out. After the 4 hours, the powders were rinsed by centrifuging the tubes at 10,000 RPM for 10 minutes, decanting the liquid, and refilling the tubes with DI water, a total of 4 times. This entire ultrasound and rinse procedure was repeated 2 more times to ensure the complete exchange of H ions for K ions. After the final rinse, the material was gently dried at room temperature to avoid the formation of other phases. XRD was used to verify the phase. The ion exchanged phase was then used to attempt pillaring of the layered structure.

C. Pillaring of H_xMnO_2

0.0643g of 4-amino-1-butanol (linear amine) and 0.0744g of 1-propanol, 3-(dimethylamino)- (tertiary amine) were each placed in a centrifuge tube with 0.2g of the ion exchanged material and DI water. The centrifuge tubes were placed in a 40kHz ultrasonic bath for 1 hour. They were then centrifuged at 10,000 RPM for 10 minutes to separate the solid and liquid, and the solid was characterized with XRD. The rest of the solid was left in the organic solutions for 24 hours to allow more time for pillaring to occur, and characterized again using XRD. The samples were placed back in the ultrasonic bath for 2 hours and gently (to avoid exfoliation) shaken every 20 minutes, and then centrifuged and characterized with XRD. After this pillaring attempt, the intercalation of Au nanoparticles into the material through an exfoliation/flocculation method was attempted.

D. Exfoliation of H_xMnO_2 and Flocculation with Gold Nanoparticles

0.35 g $H_{0.45}MnO_2$ was mixed with 2.5mL of a 1.5M TBAOH solution and 15mL of DI water to begin the process of exfoliation. The mixture was placed in a 40kHz ultrasonic bath for 3 hours and shaken every 20 minutes to facilitate exfoliation. It was then centrifuged at 10,000 RPM for 10 minutes, the liquid was decanted and kept since the exfoliated nanosheets will be in suspension, and the remaining solid was discarded. 15mL of the nanosheet liquid was mixed with 5mL of a 5nm diameter Au particle suspension. To flocculate the nanosheets, 6.0 N HCl was added to the liquid mixture at a rate of 1mL per minute until the mixture reached a pH of 1.7. Then 1.0 N NaOH was added until a pH

of 2.0 was reached. The mixture was stirred at 700 RPM for 10 minutes, and then the floccules were allowed to settle. The liquid was decanted, and the remaining solid floccules washed by adding DI water, centrifuging at 10,000 RPM for 10 minutes, and decanting the liquid a total of 3 times, to remove any remaining TBAOH from the floccules. The floccules were dried at room temperature in air and under vacuum, and characterized using XRD and a scanning electron microscope (SEM).

E. Characterization and Data Analysis

All XRD measurements were taken using a Bruker D8 Advance (Bruker, USA), with a Lynxeye XE detector and CuK α radiation (1.5406 Å). The measurement parameters for all samples were a 2θ range of 5°-70°, a step size of 0.020°, and a count time of 1.00s.

All XRD samples were prepared and measured on a single crystal sapphire zero-background holder.

SEM images and energy dispersive spectroscopy (EDS) maps were acquired using a ThermoFisher Scientific Helios FIB/SEM (ThermoFisher Scientific, USA). Samples were mounted on aluminum SEM stubs with double-sided carbon tape, and SEM images were taken with an accelerating potential of 30kV.

All XRD data processing and phase identification was performed using the software DIFFRAC.EVA (Bruker, V. 6.0.0.6). The average crystallite size of the layered

manganese oxide material with Au in the interlayer (Au-MnO₂), was calculated from its X-ray data according to the Scherrer equation, given by Equation 3:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where τ is the average crystallite size, K is a shape factor (in this case 0.89), λ is the wavelength of the X-ray beam, β is the full width half maximum (FWHM) of the XRD peak, and θ is half of the 2θ peak location. The peak location and FWHM were determined using the software Topas (Bruker-AXS, V. 6.0).

SEM images were processed using the software ImageJ (National Institutes of Health, V. 1.52a). A very rough estimation of the average diameter of particles found in one of the SEM images was determined by measuring 20 particles at random in ImageJ and averaging those measurements.

III. RESULTS AND DISCUSSION

A. Material Synthesis

The XRD data for $\text{K}_{0.45}\text{MnO}_2$ is shown in Figure 4.

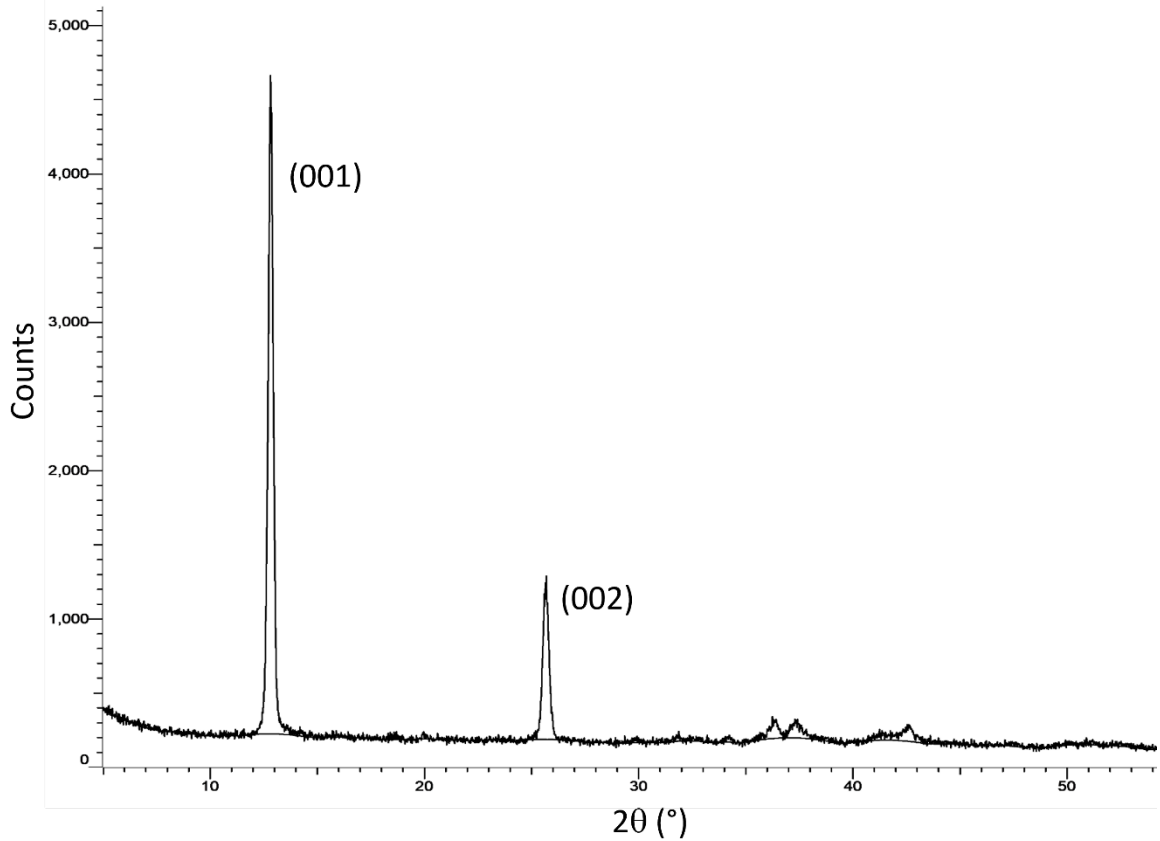


Figure 4: XRD data of $\text{K}_{0.45}\text{MnO}_2$.

The peak positions of the diffraction data in Figure 4 are consistent with the peak positions of a layered material with a known perovskite structure in the layer (Ruddlesden-Popper phase). This indicates that the desired layered phase was formed. The (001) peak labeled in the figure is an important metric in studying this material, as the (001) direction is the stacking direction. Any changes in that peak may represent a

change with the crystal ordering in that direction, indicating expansion or contraction of the interlayer. The XRD data for $\text{H}_{0.45}\text{MnO}_2$, the ion exchanged material, is shown in Figure 5, overlaid with the $\text{K}_{0.45}\text{MnO}_2$ data to compare.

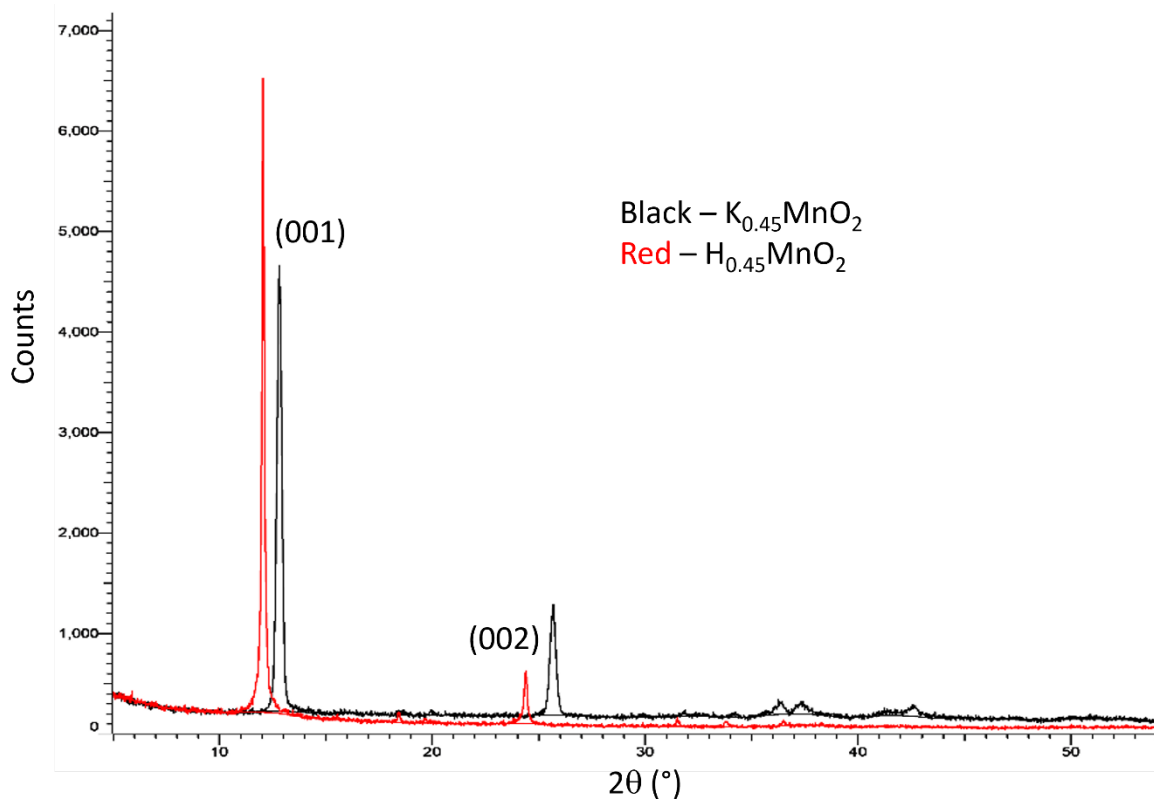


Figure 5: XRD data of $\text{H}_{0.45}\text{MnO}_2$ compared with XRD data of $\text{K}_{0.45}\text{MnO}_2$.

From Figure 5, it can be seen that the (001) peak has been significantly shifted to lower 2θ . A shift of the (001) peak to lower angle corresponds to a larger spacing between atomic planes in that direction, which in this case is the stacking direction of the MnO_2 sheets. This means that the interlayer expanded during the ion exchange, indicating that the ion exchange was successful, and the correct phase was formed.

B. Pillaring

Overlaid XRD data of the three pillaring attempts for the linear amine and tertiary amine can be seen in Figures 6 and 7, respectively. The figures show only the first peak (the (001) peak) of the data for clarity and because it is the most relevant to the discussion.

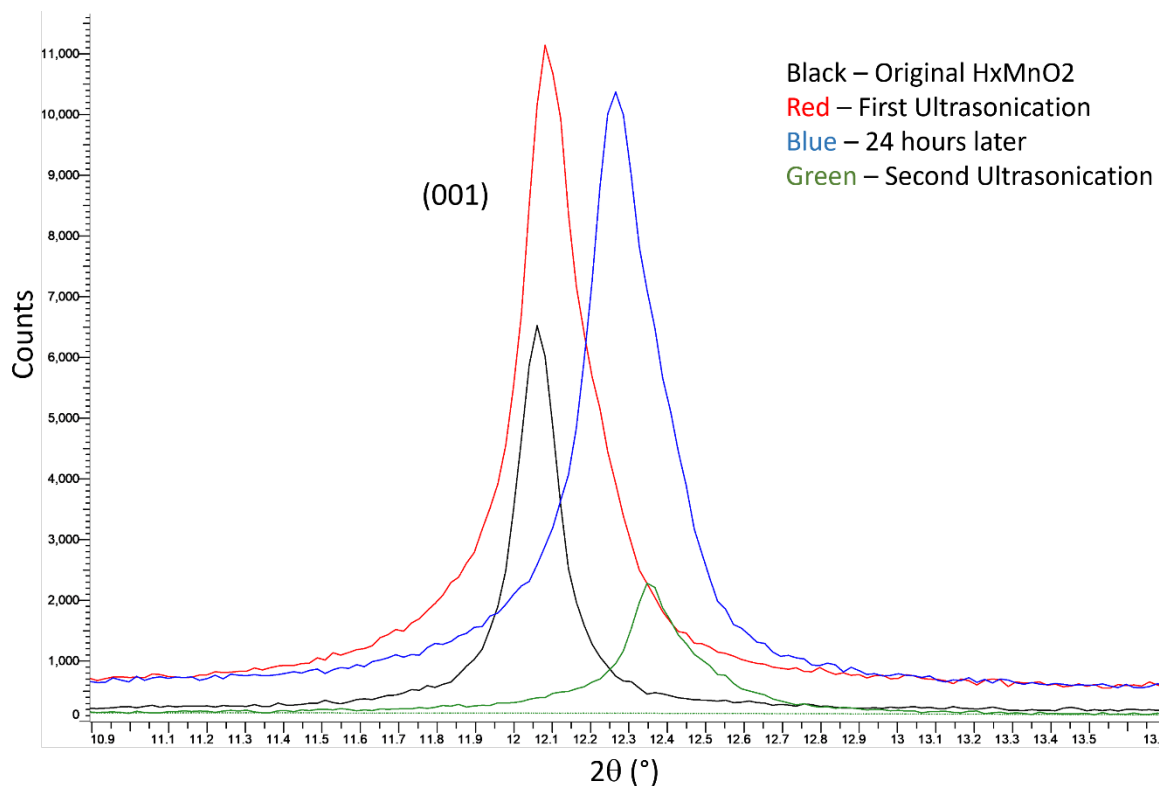


Figure 6: XRD data for the pillaring attempt using the linear amine.

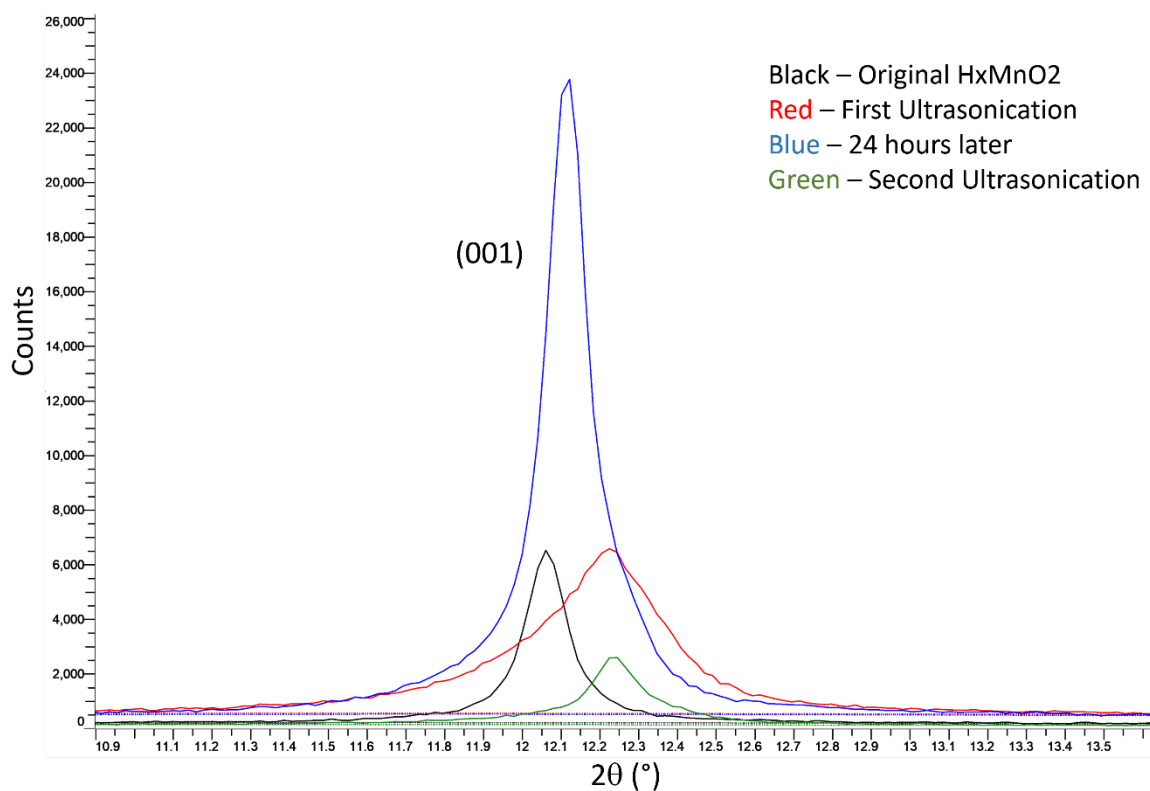


Figure 7: XRD data for the pillaring attempt using the tertiary amine.

From Figures 6 and 7, it can be seen that no appreciable peak shifting occurred after any of the pillaring steps, using either the linear or tertiary amine. Any slight shifts that are present can likely be attributed to sample displacement, as peak location is very sensitive to sample displacement at low angles. This suggests that pillaring did not occur, because if there had been expansion of the interlayer, the peak would have shifted more significantly towards lower 2θ . Additionally, after the final pillaring step, not only did pillaring not occur, but there is evidence that the material actually exfoliated. Figure 8 shows images of the linear (Figure 8a) and tertiary (Figure 8b) amine supernatants after the pillaring attempts, with a laser pointer shining through them.

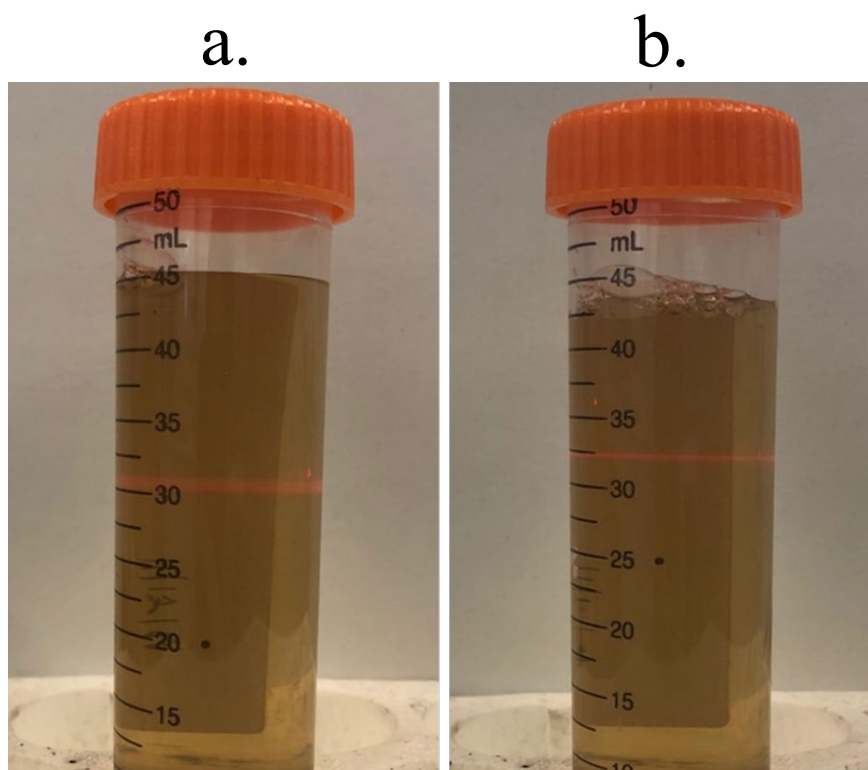


Figure 8: Laser shining through the pillaring supernatant from a) the linear amine attempt and b) the tertiary amine attempt.

First from these images, it can be seen that the color of the liquid is brownish, suggesting that there is something in the liquid, likely exfoliated MnO_2 nanosheets. This is supported by the laser pointer shining through the material. The laser can be seen within the liquid, meaning that the laser light is being scattered by something, according to the Tyndall effect. The Tyndall effect is the scattering of light by particles in a suspension or colloid, and will not occur in a true solution where molecules are dissolved. The fact that the light is scattered implies that something is in suspension, very likely the MnO_2 nanosheets, which suggests that the material exfoliated instead of being pillared.

C. Au Intercalation

XRD data of the MnO₂ sheets flocculated with Au nanoparticles can be seen in Figure 9.

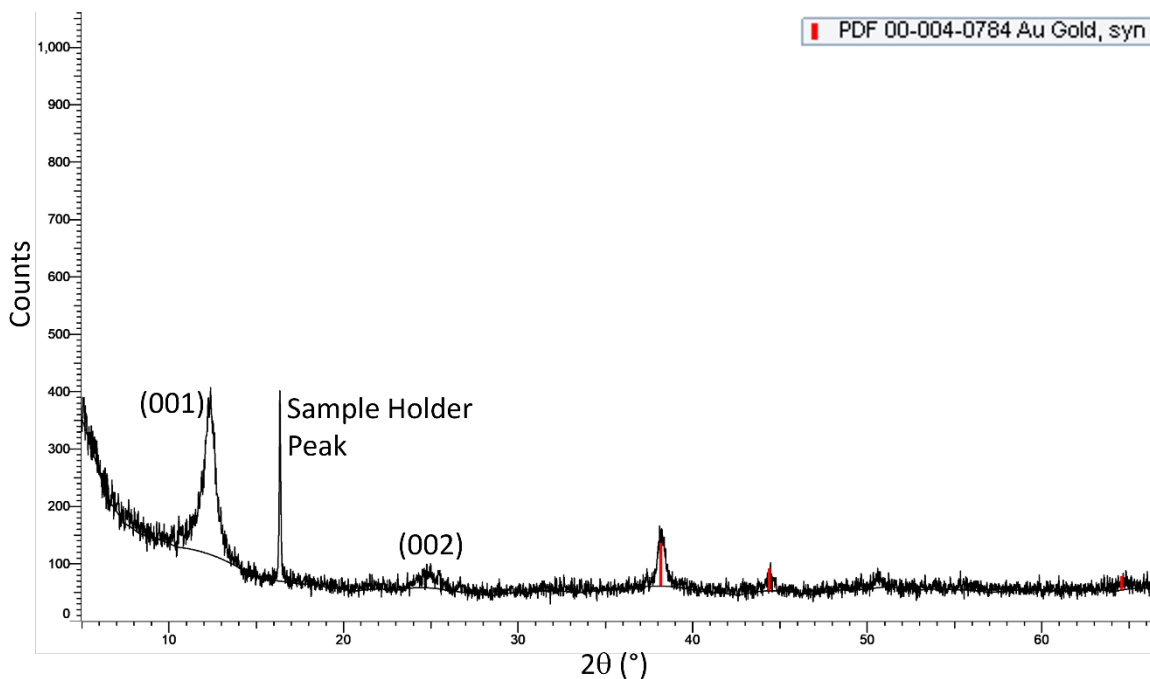


Figure 9: XRD data of the Au-MnO₂ floccules.

The data in Figure 9 shows that Au diffraction peaks are present, meaning that the gold was incorporated into the MnO₂ floccules. The other peaks and their locations are similar to the H_{0.45}MnO₂ starting material, except for the peak at around 16° 2θ. This peak was caused by an issue with the XRD sample holder, and will not be considered towards the analysis and discussion of the material. XRD data comparison of this flocculated material with H_{0.45}MnO₂ is shown in Figure 10.

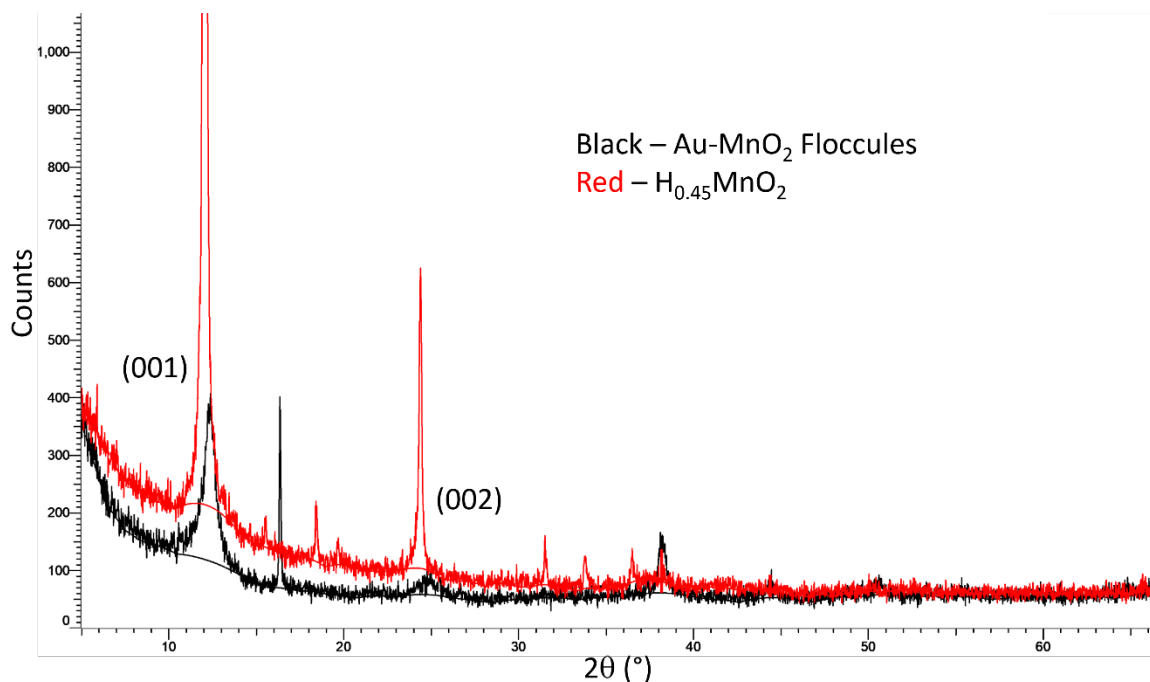


Figure 10: XRD data of the Au-MnO₂ floccules compared with H_{0.45}MnO₂.

This data shows that the peaks, especially focusing on the (001) stacking direction peak, got shorter and wider after exfoliation and flocculation, implying successful disordered restacking of the MnO₂ layers, as well as smaller crystallite size. The average crystallite size in the (001) direction was estimated to be 104Å using the full width half max (FWHM) of the (001) peak and the Scherrer equation. The parameters and result of this calculation are summarized in Table 1:

Table I: Parameters and result of the Scherrer calculation.

K	λ (Å)	β (rad)	θ (°)	τ (Å)
0.89	1.5406	0.01322	6.194	104

From the XRD data, it is clear that Au is present in the floccules, but not how the Au has been intercalated or dispersed. To determine this, and also the overall structure/morphology of the floccules, SEM and EDS analyses were performed. SEM images of air-dried and vacuum-dried Au-MnO₂ floccules are shown in Figures 11a and 11b, respectively.

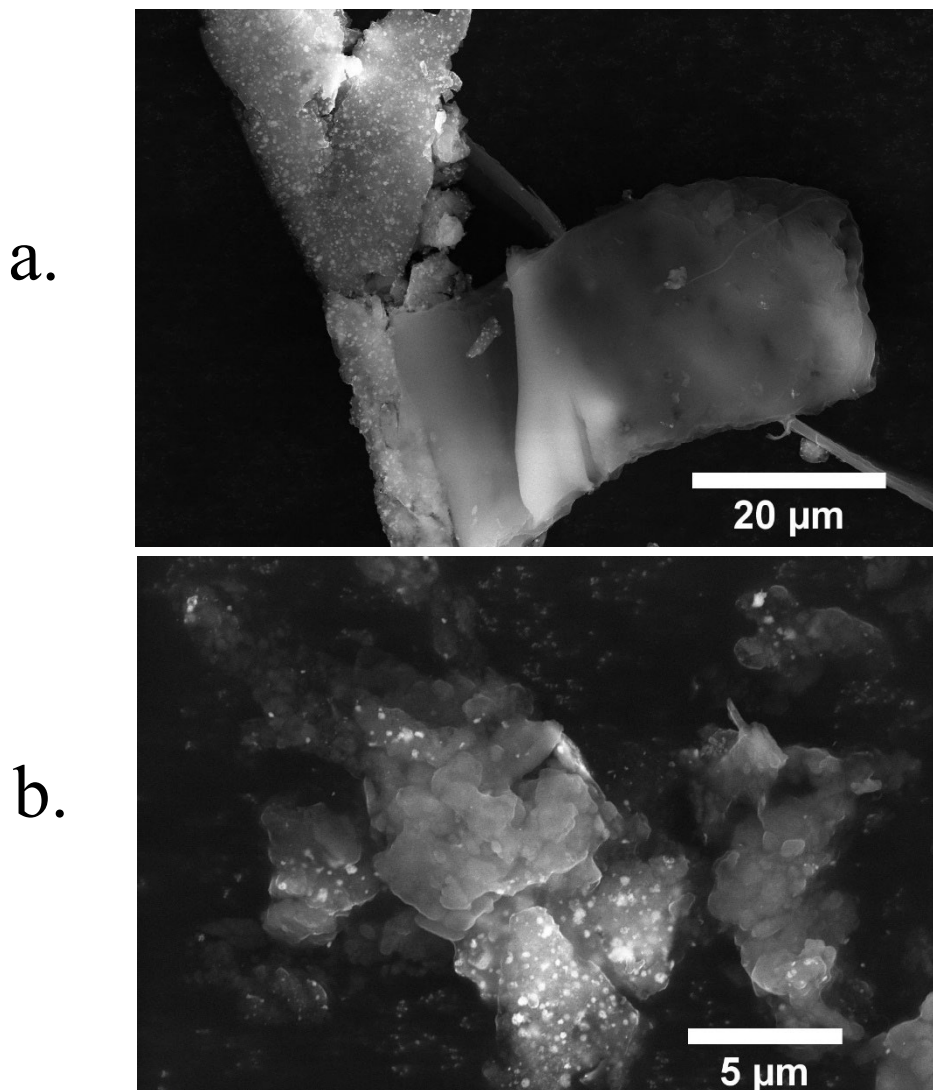


Figure 11: SEM images of a) an air-dried Au-MnO₂ floccule, b) a vacuum-dried Au-MnO₂ floccule.

These images show that the air and vacuum-dried floccules have similar structures – at least not drastically different structures. They have visible layers and sheets with particles dispersed throughout, thought to be Au particles. It seems that there is no large difference or significant effect between air drying and vacuum drying the floccules. Within the air-dried image, though, something interesting can be seen. Figure 12a is an image of the same floccule as in Figure 11a, but enlarged, and an Au EDS map of the same area is shown in Figure 12b.

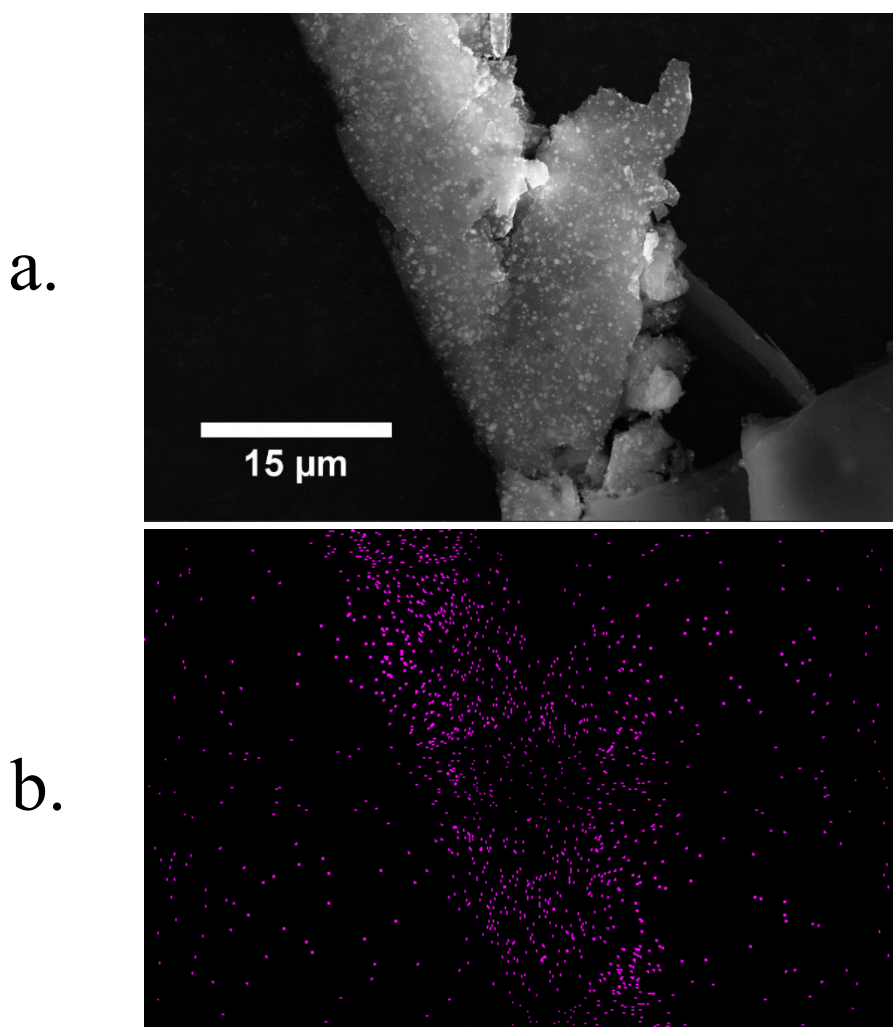


Figure 12: a) SEM image of an air-dried Au-MnO₂ floccule, b) its Au-EDS map.

The SEM image shows that there is a layered area with particles dispersed throughout, seen in the center of the figure, but there is also a layered structure with no particles, seen in the lower right-hand corner of the figure. Looking at the corresponding Au EDS map, it can be seen that there is more Au in this central, spotted area than in the lower right layered structure. This suggests that the particles dispersed in the floccules are, in fact, Au particles, and that some MnO₂ sheet restacking occurred without Au in the interlayer.

This is an interesting result, because the Au particles that were introduced before flocculation had a diameter of only 5nm, and the particles seen in the SEM image are much larger than that. The average particle diameter in Figure 12a was determined to be 259nm +/- 137nm, and while the spread is relatively large, these particles are still between 25 and 80 times larger than the 5nm diameter particles originally introduced, suggesting that the Au agglomerated during the flocculation process. This self-association of nanoparticles is not unusual, and is widespread in the literature¹⁸. So even though the Au was incorporated into the floccules, this agglomeration and the restacked portions without gold imply that it was not in a very dispersed way.

IV. CONCLUSIONS

In this investigation, the expansion of the interlayer (pillaring) in $\text{H}_{0.45}\text{MnO}_2$ using linear and tertiary amine organic molecules was unsuccessful. XRD data showed no indication of interlayer spacing change, and there was evidence supporting exfoliation of the layered material. Therefore, the hypothesis that these organic molecules lead to the expansion of the interlayer cannot be verified by this study.

The intercalation of Au nanoparticles into layered MnO_2 by an exfoliation/flocculation method appeared successful. XRD data showed that Au was present in the floccules, and EDS analysis confirmed this. However, from SEM and EDS analysis, the Au did not appear to be evenly dispersed. There was evidence that the Au nanoparticles introduced prior to flocculation agglomerated into larger particles. Also there were areas of layered, restacked MnO_2 sheets with no Au present, suggesting that an uneven distribution of the Au particles occurred. Therefore, the hypothesis that exfoliation and flocculation of MnO_2 sheets with Au nanoparticles would cause the nanoparticles to become evenly intercalated into the interlayer, cannot be verified.

V. SUGGESTIONS FOR FUTURE WORK

Much of what was attempted in this investigation is fairly new, and would benefit greatly from further research. In regard to pillaring $\text{H}_{0.45}\text{MnO}_2$, it may be interesting to try using different organic molecules to achieve the increase in interlayer spacing. Only two molecules were tried in this experiment, and there are many other viable options. If successful pillaring of the material can be achieved, it would be interesting to perform electrochemical and surface area measurements to evaluate the pillared material's potential in supercapacitor applications.

The fact that the two molecules used to attempt pillaring actually led to exfoliation is, in itself, an interesting result. TBAOH is commonly used as an exfoliating molecule, but is rather large and may not be suitable for all situations that require exfoliation. Smaller molecules, like the linear and tertiary amines used, that still exfoliate materials may be valuable for a range of uses, such as if the interlayer is too small for TBAOH to even attempt intercalation.

With the intercalation of Au nanoparticles into the MnO_2 interlayer, it would be interesting to make an electrode with the floccules and run electrochemical tests, like capacitance-voltage (CV) loops, to determine if the material has any useful electrochemical properties. It would also be beneficial to measure the surface area and see if there is any increase compared with the original layered $\text{H}_{0.45}\text{MnO}_2$. Both of these

measurements would be useful in evaluating the material as a potential candidate for supercapacitor electrodes.

Due to the potentially interesting behavior of Au nanoparticles with light, it would also be interesting to perform photocatalytic and photoelectrical properties measurements on the Au-MnO₂ layered material. These properties may be valuable for supercapacitor applications, but also many other applications where light plays an important role, such as solar cells. If these measurements do not produce any interesting results, the experimental procedure used in this investigation should be reproduced and changed in some way to prevent agglomeration of the Au nanoparticles and encourage their even dispersion in the material. The phenomenon of plasmon resonance, one of the factors that led to the selection of Au for this experiment, can only occur at metal surfaces, so the agglomeration of nanoparticles into larger particles with significant bulk material may inhibit any potentially interesting or useful light-based properties of this material. Suggestions of possible changes to the method include vigorous agitation of the mixture when flocculating, using smaller diameter gold particles, or using a more stable gold nanoparticle suspension.

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