LASER SYNTHESIS AND SPECTROSCOPY OF LIGAND-COATED TRANSITION METAL OXIDE NANOMATERIALS

by

MELISSA PRESSLEY WOODARD

(Under the Direction of Michael A. Duncan)

ABSTRACT

A laser vaporization flow reactor (LVFR) has been utilized for the gas phase synthesis of ligand-coated nanomaterials. Exploration into the gas phase synthesis of ultra-small nanoclusters and nanoparticles can help scientists understand the differences in material structure and properties in the nanoscale compared to the bulk material. The structural, electronic, and vibrational properties of nanomaterials are studied by mass spectrometry, spectroscopy, electron microscopy and computational calculations. Transition metal oxides are of particular interest due to their applications in catalysis, fuel cells, magnetic storage, photovoltaics, and other electronic devices. Chromium oxide and molybdenum oxide were studied in these synthesis experiments. Ultra-small chromium oxide nanoclusters were obtained in solution with stoichiometries not typically observed in the bulk material. We find that the complex $Cr_xO_y(MeCN)_z$ solution contains a mixture of cluster sizes and isomers making spectroscopic interpretation difficult. Molybdenum oxide nanorods were produced with a morphology unlike other molybdenum oxide nanorods made by more traditional synthetic methods. These nanorods are much smaller and have increased catalytic activity over other molybdenum oxide nanomaterials but

have optical and electronic properties similar to those of other molybdenum oxide nanorods.

INDEX WORDS: Nanoclusters, Nanoparticles, Laser Vaporization, Chromium Oxide, Molybdenum Oxide

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DEDICATION

In memory of my father, Gary Pressley.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

An important aspect in the realm of materials science is understanding the size dependent properties of materials. Nanoparticles are of interest to many scientists due to their unique size-dependent properties and the wide range of their applications. In recent years, there have been many comprehensive reviews of nanomaterials.¹⁻⁴ Nanomaterials can be made from a variety of materials, such as pure metals, metal alloys, metal oxides, organic compounds, or polymers.⁵⁻¹⁰ Two types of nanomaterials will be discussed here, nanoparticles and nanoclusters. Nanoparticles range in size from one to 100 nm and contain thousands of atoms whereas nanoclusters are on the sub-nanometer scale, are molecular in size, and may only contain up to 50 atoms.¹¹⁻¹² Nanoclusters and nanoparticles bridge the gap between atoms and bulk materials.

Due to their size, nanoclusters and nanoparticles have different electronic and optical properties compared to their bulk analogues.^{9,13-14} A classic example is gold; when gold atoms are assembled in bulk, a solid material with the familiar metallic yellow color is produced, but when assembled into nanoparticles, it can be a variety of colors. Depending on the size and shape of the gold nanoparticle, red, blue, or purple solutions can be produced. The different colors result from the difference in the optical absorption and scattering properties of the nano- sized particles. Bulk gold is considered to be a relatively inert material, but nanoparticles of gold have been shown to have significant

catalytic activity.¹⁵ Similar size dependent properties are observed in other nanomaterials such as silver, CdSe, ZnSe, TiO₂, or carbon. Because of these properties, they can be used for chemical sensors, catalysts, electronic devices, and other applications.¹⁶⁻²⁴

Nanomaterials can be produced by a variety of methods. Developing new synthesis methods and improving upon current methods to produce new types of nanomaterials is an active area of materials science research. Common nanomaterial synthesis methods are solution based reduction reactions, sol-gel methods, or hydro/solvothermal reactions.^{5-6,10,25-31} While most methods are solution based, there are some gas phase synthesis methods³²⁻³⁶ and a few based on laser vaporization.³⁷⁻⁴³

Gas phase clusters have been studied for many decades. Gas phase cluster methods use oven, arc or electrical discharges, or laser vaporization sources to bring a solid material into the gas phase.³²⁻⁴³ During laser vaporization (or ablation), a laser is focused onto the surface of a solid material where the intense energy of the laser beam ejects material from the surface of the solid producing a plasma containing neutrals, cations, anions, and electrons. Once the material is in the gas phase, a buffer gas provides collisional cooling to form atomic and molecular clusters. Clusters formed in these molecular beams are studied by mass spectrometry, electronic, or vibrational spectroscopy.^{11,44-46}

In the1980s, the Smalley group used laser vaporization to ablate a graphite target in order to study carbon clusters in a time of flight mass spectrometer, which led to the discovery of C_{60} .⁴⁷ Later, Kräetschmer and Huffman found that C_{60} was soluble in benzene,⁴⁸ could be isolated from soot, and characterized.⁴⁹ These discoveries led to a new type of nanomaterial that could be produced in the gas phase and utilized in the condensed phase. Smalley, Kroto, and Curl received the 1996 Nobel Prize for their work on C_{60} .

Transition metal oxides are of particular interest due to their applications in catalysis, fuel cells, magnetic storage, photovoltaics, and other electronic devices.^{13,18-^{22,50-58} There have been many gas phase studies of transition metal oxide clusters including oxides of titanium,⁵⁹⁻⁶⁰ vanadium,⁶¹⁻⁸¹ chromium,^{60,82-91} iron,⁹²⁻⁹³ manganese,⁹⁴ cobalt,⁹⁵⁻⁹⁶ nickel,⁹⁶ yttrium,⁹⁷ niobium,^{66,68,72,98} molybdenum,^{85,99-110} tantalum,^{66,68,72} lanthanum,⁹⁷ cerium¹¹¹ and many others.¹¹²⁻¹¹⁴ These studies investigated both neutral and ionic clusters and have provided insight into the geometric and electronic structures, bonding and dissociation energies, and catalytic reactions with small molecules and hydrocarbons. Many of these studies observe unique stoichiometries in the gas phase that are typically not the same as those in naturally occurring bulk material.}

Unlike C_{60} , many interesting clusters produced in the gas phase have not been successfully brought into the condensed phase. Since these gas phase studies can produce stoichiometries not observed in the bulk, it is of interest to develop a method that can produce these clusters for use outside of the gas phase. Our research group has developed a laser vaporization flow reactor (LVFR) to synthesize ligand-coated nanoclusters and nanoparticles.¹¹⁵⁻¹¹⁷ This method utilizes laser vaporization to grow nanoclusters and/or nanoparticles in the gas phase, ligand coat them, then condense them into the solution phase. Successful LVFR synthesis experiments include the production of titanium and titanium oxide nanoclusters coated with ethylenediamine (en) or tetrahydrofuran (THF) ligands,¹¹⁵ vanadium oxide nanoclusters coated with THF or acetonitrile (MeCN) ligands,¹¹⁶ and silver nanoparticles coated with MeCN ligands.¹¹⁷ The material is

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characterized with a variety of analytical techniques including but not limited to: laser desorption (LD) or electrospray ionization (ESI) time of flight mass spectrometry (TOF-MS), UV/Visible, fluorescence, infrared and Raman spectroscopy, electron microscopy for imaging larger nanoparticles, and catalytic activity tests. Theoretical calculations, using density functional theory (DFT) in the Gaussian09 software program,¹¹⁸ are performed for ultra-small nanoclusters to predict structures, relative energies, and vibrational and electronic spectra for comparison to experimental data.

Vanadium oxide is a prime example of the differences in stoichiometries found in bulk material versus those that are produced in the gas phase. Bulk vanadium oxide has a stoichiometry of V₂O₅, however there have been several gas phase studies on vanadium oxide that observe stoichiometries other than the bulk V_2O_5 .^{61-71,74-79,119-121} Our group studied the photodissociation of vanadium oxide clusters in the gas phase with mass spectrometry and determined the most stable stoichiometries to be $V_2O_4^+$, $V_3O_7^+$, $V_4O_9^+$, $V_5O_{12}^+$, $V_6O_{14}^+$, $V_7O_{17}^+$, 72 Later, vanadium oxide was studied in the LVFR synthesis apparatus to determine if these gas phase clusters could be ligand-coated and brought into the condensed phase.¹¹⁶ In separate synthesis experiments, acetonitrile (MeCN) and tetrahydrofuran (THF) were used as ligands. A wide variety of stoichiometries with ligand coating were observed in the LD-TOF MS spectra. The prominent peaks were assigned to V₃O₆(MeCN)₂, V₄O₉(MeCN)₂, and V₅O₁₂(MeCN)₃ which were consistent with the stoichiometries observed in previous photodissociation experiments. DFT calculations indicated the same cluster structures as in the gas phase but with MeCN ligands attached at a metal site with a terminal oxygen. By changing the ligand to THF, a high abundance of the $V_3O_4(THF)_3$ cluster was observed almost exclusively, the structure of which appears the same as the V₃O₇ cluster with the THF ligands binding through oxygen substitution at the terminal sites. This experiment demonstrates the ability to capture metal oxide clusters with various stoichiometries in the condensed phase. Expanding upon this work, the synthesis and characterization of ligand-coated chromium oxide nanoclusters¹²² and molybdenum oxide nanorods were studied and are the focus of this dissertation.

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CHAPTER 2

EXPERIMENTAL SETUP

Synthesis of ligand coated cluster materials occurs in the laser vaporization flowtube reactor (LFVR), which has been previously described and successfully used to produce ligand coated metal or metal oxide nanoclusters¹⁻² or nanoparticles.³ The LFVR uses a high power, high repetition rate laser to ablate material from a rotating metal rod into the gas phase under carrier gas flow. Once clusters are in the gas phase, ligands are added and material is collected in a liquid nitrogen cooled trap, as shown in Figure 2.1.

The top of the apparatus, labeled Region 1 in Figure 2.1, is a water cooled sixway cross where the rotating metal rod, vaporization laser, and carrier gas are introduced and cluster production begins. The vaporization laser is a Coherent LPX Pro 240F excimer laser with a wavelength of 248 nm (KrF). The laser can operate at repetition rates from 10-400 Hz with laser power ranging from 60-190 mJ/pulse. The spot size of the laser is focused to a roughly 3 x 12 mm rectangle along the length of the metal rod. These laser conditions are varied and optimized based on the metal system studied. An inert gas, typically helium, is used as the carrier gas for pure metal systems while seeded gas mixtures (typically with 1-10% oxygen in helium) are used for metal oxide systems. An Edwards E2M40 mechanical pump is used to first evacuate the chamber to a pressure of 1 x 10^{-3} torr. Then the carrier gas is added until the chamber reaches the desired pressure, typically 10-15 torr, depending on the experiment. The gas is continually expanded through a 750 μ m hole above the metal rod and flows over the length of the rod through the plasma created by the vaporization laser. The carrier gas provides an oxygen source for metal oxide production as well as collisional cooling for cluster growth. Clusters grown in this section of the apparatus then pass through an aperture (1/2 in.)diameter) into the ligand addition region, labeled Region 2 in Figure 2.1. The apertures slow the flow rate in this region to promote ligand addition. Ligands are typically added as the vapor pressure above the solvent is entrained in argon, but aerosols produced from a nebulizer or an oven source can be used to introduce ligands with very low vapor pressure or solids. Acetonitrile is the ligand of choice for metal oxide systems due to the high vapor pressure and ease of use with the apparatus. The clusters then flow through a second aperture (1/4 in. diameter) into the liquid nitrogen cooled trap (77 K) comprised of a round bottom flask filled with glass beads, labeled Region 3 in Figure 2.1. The beads provide many cold surfaces to promote condensation and collection of the material. Experiments run for several hours. Once complete, the flask is removed and the collected material is warmed to room temperature under an argon flow, resulting in a solution with ligand coated clusters. The amount of material produced varies with the metal system studied but ranges anywhere from fractions of a milligram up to a few milligrams per hour.

Ligand coated cluster samples are then characterized by a variety of analytical methods. Laser desorption time of flight (LD-TOF) and electrospray ionization time of flight (ESI-TOF) mass spectrometry are used to determine the size and stoichiometries of the clusters in solution. While ESI-MS and MALDI-MS (matrix assisted laser desorption ionization mass spectrometry) are widely used and commercially available techniques,

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neat laser desorption is less common but has a well-established history.⁴⁻⁸ Though these two mass spectrometry methods provide similar mass analysis, they proceed with different ionization methods.

Electrospray ionization mass spectrometry is utilized for liquid samples, can produce singly or multiply charged ions, and is fairly well understood.⁹⁻¹⁰ Ionization takes place by pumping the liquid solution through a charged capillary to form a Taylor cone of charged droplets. The droplets become smaller and smaller, through solvent evaporation and Coulomb repulsion, until gas phase ions are produced and are then sent into the mass spectrometer (Figure 2.2).

Laser desorption mass spectrometry is used for solid non-volatile samples and typically only produces singly charged ions. The ionization process is not as well understood and multiple processes may be taking place simultaneously.^{4-5,8,11-12} To desorb and ionize the sample, a pulsed laser is focused onto the surface of the sample, the energy of which, vaporizes the sample and creates a plume of material containing ions, electrons, and neutrals (Figure 2.3). Ionization most likely occurs from a combination of multiphoton photoionization and electron impact ionization. Multiphoton ionization is possible due to the large number of photons emitted with each laser pulse. Most molecules have ionization potentials between 7 and 12 eV which would require multiple photons to ionize the sample given that the UV and visible lasers used in these experiments can provide single photons with 1.17 eV (1064 nm), 2.33 eV (532 nm), 3.49 eV (355 nm), or 4.66 eV (266 nm) of energy. Electron impact ionization could also be taking place simultaneously. Thermionic emission and the photoelectric effect can produce electrons from the heated sample or the metal sample probe tip, that when

accelerating within the source region, can ionize the sample. Other ion-molecule reactions may also be taking place within the sample plume. Though it is difficult to determine one specific ionization process taking place, our group and others have shown that LD-TOF MS is suitable for a wide variety of samples including fullerenes,¹³⁻¹⁸ PAHs (polycyclic aromatic hydrocarbons)¹⁹ and metal-PAH complexes,²⁰⁻²¹ organic and biological molecules,²²⁻²³ and metals or other inorganic compounds.^{11,19} MALDI operates with the same experimental set up as LD but is typically utilized for high mass biological samples, where an organic acid matrix is used to absorb the UV laser radiation instead of the sample of interest. Ionization occurs from proton transfer from the matrix to the sample.^{9-10,24-25}

In the laser desorption analysis of our materials, the sample solution is dried onto a probe tip, inserted into the mass spectrometer, and either the 2nd (532 nm, green) or the 3rd (355 nm, UV) harmonic of a Nd:YAG laser (New Wave Research Polaris II) is used to desorb and ionize the sample. In our lab, we have two LD-TOF mass spectrometers. The first is a home-built spectrometer¹¹ ("Null App") which is optimized for higher mass range but lower resolution with an EMT detector. The second is a Comstock LD-TOF MS which is optimized for a lower mass range but higher isotopic resolution with an MCP detector. Both mass spectrometers have a Wiley-McLaren design²⁶ and have the capability to operate in linear or reflectron mode.²⁷ In our lab, we typically use these mass spectrometers to analyze cations. However, when necessary, they can be switched over to analyze anions. This requires switching the power supplies controlling the electrodes to produce negative voltages instead of positive. For the types of samples discussed in this work, similar spectra are observed whether using green or UV wavelengths for desorption. Although there are systems where a specific desorption wavelength provides more efficient ionization. A range of laser desorption powers are used to identify "gentle" conditions that do not induce a large amount of fragmentation of our sample. Typically, our desorption laser powers are 1 mJ/pulse or less due to fragmentation observed at higher laser powers. In addition to fragmentation, cluster growth can also occur in the laser desorption plume. To determine if the peaks observed in the mass spectrum are from clusters synthesized in the flow reactor or within the mass spectrometer itself, a control sample of bulk material is analyzed for comparison. If needed, the MALDI matrix 2,5-dihydroxybenzoic acid (DHB) is used for samples where neat laser desorption is ineffective.

ESI analysis on either a Mariner Biosystems or a Waters LCT Premier mass spectrometer provides the ability to directly inject our solution into the instrument. These instruments use reflectrons and MCP detectors which result in higher resolution spectra. With the high resolution, we can use simulated isotope distributions, simulated with Isopro 3.1,²⁸ for confirmation of mass assignments (Figure 2.4). The spectra discussed here collected from the Mariner and Waters instruments, were acquired in "V Mode". This utilizes the reflectron to produce a V shaped ion path, as shown in the middle panel of Figure 2.2. The Waters LCT Premier has an additional option for "W Mode", where a lens is used to turn the ions back into the reflectron, creating a W shaped ion path (bottom panel, Figure 2.2) and further increasing the mass resolution.

Commercial ESI instruments easily provide the ability to analyze both cations (positive mode) and anions (negative mode) for our samples. We utilize both modes for a

complete analysis of our sample with ESI and there are advantages and disadvantages to both. In negative mode, the spectra tend to have less background noise compared to the positive mode spectra. However, the spray in negative mode can produce a corona discharge and ionization of the atmosphere can occur which could introduce contamination and obscure the sample peaks in the spectrum. The corona discharge can be prevented by flowing an electron scavenger such as O_2 or SF₆ alongside the spray, using chlorinated solvents, or as in our instrumental design using a nebulization gas for droplet formation.^{10,29} As will be discussed in the following chapter on chromium oxide, we typically see similar cluster sizes with both types of ionization, but we do observe more ligand stripping with ESI than with LD ionization and we typically observe more fragmentation in negative mode ESI than in positive mode ESI.

When the mass spectrum indicates smaller nanoclusters are present in solution, density functional theory (DFT) and time dependent density functional theory (TD-DFT) in the Gaussian09 software package³⁰ are used to calculate optimized structures and relative energies of various isomers. The predicted spectra from these calculations are used for comparison to experimental results. However, due to the size of our metal oxide clusters, we are limited to lower level DFT calculations and can only calculate clusters with a limited number of ligands.

Larger nanoparticles can be present in the solution in addition to or instead of smaller nanoclusters. To investigate the presence of larger nanoparticles, electron microscopy is used for imaging (TEM FEI Tecnai 20) and elemental composition (STEM/EDS FEI Teneo) of the particles. Small nanoclusters cannot be imaged but larger nanoparticles (5 nm and up) can easily be detected in the TEM.

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The optical properties of the solution are evaluated using absorption (Shimadzu UV-2600), emission (Shimadzu RF-5301C), infrared (Nicolet 6700 FTIR, diamond ATR) and Raman (Renishaw inVia Raman Microscope, Thermo DXR Raman Microscope) spectroscopy.

Though our main focus is on the synthesis of new and interesting ligand coated nanomaterials, not on the application of the materials, we do analyze the catalytic activity of systems that have been shown in the literature to be suitable catalysts. We do this by a simple well-established dye degradation test.³¹⁻³³ We add our dried material to a methylene blue solution and spectroscopically monitor the degradation of the dye (color change from blue to clear) under UV irradiation.

The experimental results are compared to reports in the literature for both the bulk and nanomaterials synthesized by other methods. If possible, a commercial material is also obtained for a direct comparison and analyzed alongside our synthesized material.

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Figure 2.1. Schematic of LVFR apparatus.



Figure 2.2. Electrospray ionization time of flight mass spectrometry source region (top panel). Cation production is depicted but negative voltages can be applied to the tip for production of anions. The basic schematic of an instrument in V mode is shown in the middle panel. Spectra shown in this dissertation were collected in V mode. The Waters LCT Premier also has a W mode option (bottom panel).



Figure 2.3. Laser desorption time of flight mass spectrometer schematic in reflectron mode (top panel) and linear mode (bottom panel). The Comstock and Null App can be used in linear or reflectron mode. Major differences between the two instruments include detectors, deflectors, and pumps. The Comstock has MCP detectors, horizontal and vertical deflection plates, and turbomolecular pumps. Null App has an EMT detector, horizontal deflection plates, and diffusion pumps.


Figure 2.4. Simulated isotopic distributions (Isopro 3.1) of Cr_n (top) and Mo_n (bottom) clusters where n=1-3.

CHAPTER 3

LASER SYNTHESIS AND SPECTROSCOPY OF LIGAND-COATED CHROMIUM OXIDE NANOCLUSTERS

Introduction

Chromium oxide nanoparticles and clusters have been studied in solution, on surfaces, and in the gas phase.¹⁻⁶ They have many interesting properties that make them suitable for use in catalysis, chemical sensors, and electronic materials. Gas phase experiments have probed these clusters with mass spectrometry,⁷⁻¹² photodissociation,¹¹ photoelectron spectroscopy,¹³⁻¹⁷ as well as infrared spectroscopy on matrix isolated clusters.¹⁸ There have been extensive computational studies carried out by various groups.^{10,12,14-17,19-25} Results from these efforts have determined stable stoichiometries of these small chromium oxide clusters and found that they are unlike the stoichiometries of common bulk chromium oxide materials. Multiple experiments are in agreement and find clusters of $Cr_2O_4^+$, $Cr_3O_6^+$, $Cr_3O_7^+$, and $Cr_4O_{10}^+$ are grown reproducibly and have shown that neutral clusters of CrO₃, Cr₂O₅, and Cr₄O₁₀ are eliminated during photodissociation.⁷⁻ ¹¹ In our photodissociation experiment, these same observations were made and the Cr₄O₁₀ cluster was the most prominent cation in the mass spectrum.¹¹ The stability of these chromium oxide clusters and their similarity to the vanadium oxide clusters discussed in Chapter 1 make them suitable candidates for synthesis and ligand coating within the LVFR apparatus.

Experimental

Ultra-small ligand-coated chromium oxide nanoclusters were produced in a laser vaporization flow tube reactor as previously described.²⁶⁻²⁸ A chromium rod was ablated with a high power high repetition rate KrF excimer laser (Coherent LPX Pro 240F or Lambda Physik Compex 102, 248 nm) focused to a spot size of 3 x 12 mm under a flow of O₂ in helium. Acetonitrile ligands were entrained in argon vapor and injected into the gas flow. The gas flow was condensed in a liquid nitrogen cold trap (77 K). The synthesis was run for one to two hours. After synthesis, excess ligand was added into the trap before removing from the apparatus. The frozen material was warmed under a flow of argon and resulted in a brown solution. A variety of experimental conditions were explored but held constant within a single experiment. Ligand-coated chromium oxide nanoclusters were produced with laser powers ranging from 100 ("low") to 180 ("high") mJ/pulse, repetition rates from 100-400 Hz, oxygen partial pressure ranging from 5-10%, and pressure within the chamber ranging from 2-15 torr.

Analysis of the solution was done using a variety of techniques. To investigate cluster sizes and stoichiometries, laser desorption (LD) and electrospray ionization (ESI) time of flight mass spectrometry (TOF-MS) was used. For laser desorption analysis, the sample solution was dried onto a stainless-steel probe tip and inserted into a homemade time of flight mass spectrometer. A pulsed Nd:YAG (532 nm, New Wave Research Polaris II) was used to desorb and ionize the sample. For ESI analysis, the sample solution was directly injected into a Mariner Biosystems mass spectrometer. Optical properties were explored with absorption spectroscopy (Shimadzu UV-2600), fluorescence spectroscopy (Shimadzu RF-5301C), infrared spectroscopy (Nicolet 6700

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FTIR, diamond ATR) and surface enhanced Raman spectroscopy (SERS) (Renishaw inVia Raman Microscope) using specially prepared silver nanorod arrays.²⁹ Imaging of the sample with transmission electron microscopy (TEM) (FEI Tecnai 20) was used to look for larger nanoparticles.

Extensive computational calculations were performed with density functional theory (DFT) and time dependent density functional theory (TD-DFT) in the Gaussian09 software program.³⁰ The BP86 functional³¹⁻³² and TZVP basis set³³ were used for the majority of calculations; however, due to the size and difficulty in calculations for some of the larger clusters a smaller double zeta basis set³⁴⁻³⁶ was employed. These calculations were used to determine isomeric structures, relative energies, ligand binding energies, and predicted spectra. Predicted vibrational spectra are presented without scaling and using simulated linewidths of 50 cm⁻¹. Predicted optical absorption spectra from TD-DFT calculations are presented with linewidths of 20 nm for comparison to experimental spectra.

Results and Discussion

The frozen material in the trap was warmed under a flow of argon and resulted in a brown solution. The solution was filtered to remove any insoluble material; only the soluble portion of the collected material was characterized. Control LVFR experiments, "ligand only" or "clusters only" did not result in soluble material for analysis. The experimental results from the material characterization were compared to the predicted spectra from the DFT calculations and to the results of previous reports for other chromium oxide bulk and nanomaterials, the comparison of which is discussed in the

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following sections. As a matter of notetaking, a generic notation for the solution is referred to as $Cr_xO_y(MeCN)_z$. Specific clusters will be discussed as (x,y) for bare clusters and (x,y,z) for ligand-coated clusters. For example, the notation $Cr_3O_7(MeCN)_2$ and (3,7,2) represent the same cluster and (3,7) represents the bare cluster.

Nanoparticle/Nanocluster Determination-Mass Spectrometry

Mass spectrometry and TEM imaging were used to determine if small molecular size nanoclusters or larger nanoparticles were produced. The presence of larger nanoparticles was not detected by TEM imaging. There were trace amounts of larger nanoparticles observed but not enough to be considered significant. Both laser desorption and electrospray ionization mass spectrometry were used to investigate the presence of smaller nanoclusters. During laser desorption analysis, the desorption laser power was varied throughout to determine optimal conditions where fragmentation of the sample is limited; this threshold was around 1 mJ or less per pulse. The laser desorption mass spectrum shown in Figure 3.1 was collected from a "medium" laser power synthesis run (140 mJ/pulse). We observed prominent stoichiometries of Cr_xO_v of (2,4), (3,7), (4,10), (5,14), and (6,14) with various amounts of ligand coating. These stoichiometries differ from the bulk chromium oxide Cr_2O_3 , which is a green powder commonly used as a pigment. In control experiments, where bulk chromium oxide is mixed with acetonitrile and analyzed under the same mass spectrometer conditions, only Cr^+ and CrO^+ peaks were observed. Therefore, we conclude that the observed experimental spectrum results from the soluble material produced during LVFR synthesis.

Although we observe a distribution of cluster sizes, we also observed that the abundant cluster sizes produced increased with an increase in synthesis laser power when the mass spectrometer conditions are just above the threshold for signal detection (0.5 mJ/pulse). As shown in Figure 3.2, material produced with "low" laser power (100 mJ/pulse) has a higher abundance of the (4,10) cluster compared to larger cluster sizes, while "medium" laser power (130 mJ/pulse) produces a greater abundance of (5,14) relative to other cluster sizes. At "high" laser power (170 mJ/pulse) we observe a higher abundance of the (6,14) cluster relative to the other cluster sizes.

We also analyzed the samples by ESI-TOF MS in positive and negative mode. The positive ion spectrum shown in Figure 3.3 contains peaks with stoichiometries similar to those observed in the LD-TOF MS. ESI provides spectra with isotopic resolution (as discussed in Chapter 2) which can be used to confirm mass assignments based on simulated isotope patterns, as simulated in the IsoPro 3.1 program³⁷ and shown in Figure 3.4.

We notice some differences between the ESI and LD spectra. In particular the (5,12) cluster was more abundant in the ESI than in the LD mass spectrum, where the (5,14) cluster is more abundant and there are overall fewer ligands on the clusters in the ESI spectrum. We attribute these differences to the nature of ionization in the two kinds of mass spectrometers. Electrospray ionization causes more fragmentation of our material than laser desorption ionization. We also analyzed the material in ESI negative mode and observed more extensive fragmentation of our sample. We observed only $(CrO_3)_n^-$ clusters with no attached ligands.

Though we take precautions to minimize fragmentation during both LD and ESI analysis, we cannot definitively say that there is no fragmentation occurring during the ionization process. However, we believe that the clusters observed in the LD spectrum best represent clusters present in the sample solution and in particular the core metal oxide stoichiometries. The metal-oxide bonds are expected to be much stronger than the metal-ligand bonds, so fragmentation by the loss of ligands is more likely than metal-oxide decomposition. The stoichiometries observed here are consistent with the those observed in previous laser vaporization gas phase experiments.⁹⁻¹¹ The prominent clusters in the mass spectra of those experiments were the (4,10), (5,12), (5,13), (6,14), (7,17), (8,19) (9,22) cation clusters. Photofragmentation experiments produced stable clusters of (2,4), (3,7), (4,10), (5,11), (5,12), (6,14) and (7,17) cations with (1,3), (2,5) and (4,10) as neutral leaving groups.¹¹

Computational Studies

Computational studies to investigate cluster geometries, relative energies, and predicted spectra used the Gaussian09 software program³⁰ with density functional theory at the BP86/TZVP level for most cluster sizes.³¹⁻³³ For some of the larger ligand-coated clusters a double zeta basis set³⁴⁻³⁶ was used due to the computational expense. There have been several previous computational studies on chromium oxide cluster as well.^{10,12,14,16-17,19-23} The neutral clusters of (2,2), (2,4), (3,7), (4,10), (5,12), (5,14) and (6,14) were investigated in the singlet, triplet, quintet, septet, and nonet spin states. The most stable isomer(s) of the cluster size were also calculated with various numbers of ligands as well as different cation charge states. No algorithms were used for

systematically searching structures. Structures were generated manually as well as from structures presented in other metal oxide cluster studies. Please refer to the Supporting Information associated with the published manuscript for extensive details and figures not shown here.³⁸ The lowest energy isomers of the bare and ligand-coated clusters are presented in Figure 3.5, 3.6, and 3.7, as well as their relative energies in Table 3.1. Structures for the (2,4), (3,7) and (4,10) clusters were consistent with previous reports.^{10,12,14,16-17,19-23} We find that there are "cage", "ring", and "chain" like isomers for each cluster size, with the number of each increasing with the cluster size. For most clusters the compact cage structure is most stable with the exception of the (5,14) species. Here we observed that more open ring structures. Structures of the cations were approximately the same as those of the neutral clusters with only minor differences in bond lengths and angles and in only a few clusters did the spin state significantly change the structure.

The ligand binding energy was also calculated and is presented in Table 3.1. Ligand binding was found to occur on the metal site having a terminal oxygen, which is consistent with the acetonitrile ligand binding in ligand-coated vanadium oxide clusters.²⁷ The binding energy was calculated to be 20-30 kcal/mol. With binding energy values in this range, ligand loss during mass spectrometry is not unreasonable. For some cluster sizes, the ligand binding does change the spin state of the lowest energy isomer. For example, the lowest energy bare (2,2) cluster is in a nonet state, but upon addition of four ligands (2,2,4) the spin state is a triplet. In the (2,4) cluster, the most stable bare cluster is a triplet, where all the lowest energy ligand coated clusters are singlets. The lowest energy cage structure of the (3,7) cluster is a quintet, but upon addition of one ligand the lowest energy spin state was a singlet. Addition of two or three ligands changed the spin state to a triplet.

Electronic Spectroscopy

Further characterization of the solution was done by various spectroscopy techniques. In the UV/Visible absorption spectrum of the $Cr_xO_y(MeCN)_z$ solution, in the blue trace shown in Figure 3.8, we observed strong peaks at 365 and 266 nm with weak features in the visible region. These transitions are consistent with the absorption profiles of other chromium oxide materials.¹⁻⁶ Diffuse reflectance measurements of bulk Cr_2O_3 indicate absorption in the 460-470 nm and 590-620 nm regions.⁶ Highly oxidized materials with chromium in the +6 oxidation state have transitions in the 360 and 260 nm regions associated with the metal-oxygen charge transfer.¹⁻² Our sample does not have strong absorptions in the visible region that is observed in the bulk Cr_2O_3 where chromium is in the +3 oxidation state but is consistent with the absorption observed in highly oxidized chromium oxides. The clusters we observed (2,4), (3,7), (4,10), (5,12), (6,14) have oxidation states of +4, +4.7, +5 +4.8, and +4.7, respectively.

We also compared the observed absorption to photoelectron spectroscopy (PES) results reported by Wang and coworkers.¹⁴⁻¹⁶ They studied the electron affinity of anion chromium oxide clusters and the electronic states of the neutral clusters produced by photodetachment. They studied a variety of cluster sizes but only the (2,4) and (4,10) clusters overlap with our observed clusters. The excited states found for the (2,4) and (4,10) clusters are shown by the green and purple lines, respectively, in Figure 3.8.

Unfortunately, the PES experiment cannot provide intensity information relevant for comparison to our UV/Visible spectrum. The (2,4) cluster had transitions at 670 nm $(X\rightarrow B)$, 450 nm $(X\rightarrow C)$, 360 nm $(X\rightarrow D)$. The X \rightarrow A transition occurred at 970 nm and falls outside the range our experimental UV/Visible spectrum. The only transition for the (4,10) cluster that falls within the range of our UV/Visible spectrum was the X \rightarrow C transition at 390 nm.

We also compared the experimental spectrum to spectra predicted by TD-DFT computations for bare clusters, shown in Figure 3.9. The selected structures have absorption features in the UV region of interest but no one cluster matches the experimental spectrum (please refer to the Supporting Information of the published manuscript for spectra of all calculated cluster sizes). For example, the (4,10) cluster has bands predicted at 360 and 260 nm that correspond to our experimental spectrum, but we did not observe the band predicted at 510 nm. The larger (5,14) and (6,14) clusters also had absorption in the UV region, but the band predicted at 410 nm was also not observed in the experimental spectrum.

We explored the effects of ligand binding on the spectra, as shown in Figure 3.10. Previous work³⁹⁻⁴⁵ and the calculations presented here, have shown that ligand binding affects the electronic structures, spin states, and spectra of these clusters. For example, the lowest energy cage structure of the (3,7) cluster is a quintet but upon addition of one ligand the lowest energy spin state becomes a singlet and the addition of two or three ligands changes the spin state to a triplet. We observed peak shifts and broadening in the spectra predicted for the ligand coated clusters compared to those of the bare cluster. Ligand binding cannot be fully explored due to the limitations of the DFT calculations. For larger clusters we are unable to calculate a structure with more than two ligands. Therefore, it is likely that there are structures whose spectra cannot be investigated.

Even though there is not a definitive match between theory and experiment, we do observe an experimental UV/Visible absorption spectrum similar to those of other chromium oxide materials. The spectrum is consistent with highly oxidized chromium oxides represented by the absorption peaks at 365 and 265nm. Preliminary investigation into the separation of the cluster sizes was done with high performance chromatography (HPLC) which also indicated a complex mixture of several components. We also explored fluorescence of the material by exciting the sample at 355 nm. We observe emission at 463, 419, and 397 nm as shown by the red trace in Figure 3.7. The sharp peak at 397 nm corresponds to acetonitrile and the other broad emission observed is due to the chromium oxide clusters.

Vibrational Spectroscopy

The infrared and Raman spectra were collected to obtain further insight into the structures of the clusters produced. The infrared spectrum, shown in Figure 3.11, was collected by attenuated total reflectance (ATR) by dropping and drying the sample directly onto the diamond ATR crystal. Comparison to the predicted spectra of bare clusters, shown in Figure 3.11, did not provide a clear match to the experimental spectrum (please refer to the Supporting Information of the published manuscript for spectra of all calculated cluster sizes). Again, being aware of ligand addition effects, we also compared to the predicted spectra of ligand-coated clusters (Figure 3.12). As with the electronic spectra, we also observed a vibrational shift upon ligand addition. For

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example, the bare (5,14) fused bicyclic structure does not have a peak in the 740 cm⁻¹ region but the ligand coated (5,14,2) fused bicyclic structure does. In the bare clusters, the Cr=O stretch in the 1030-1060 cm⁻¹ region shifts to higher frequency upon ligand addition.

The larger more open (5,14) fused bicyclic, spiro-bicyclic and ring clusters have peaks in the 740 and 840 cm⁻¹ regions, similar to the experimental spectrum, that are not observed in the smaller more compact clusters. In the experimental spectrum, the peak at 740 cm⁻¹ corresponds to the Cr-O-Cr breathing motion in the cluster framework, as observed in the (5,14,2) fused bicyclic and spiro-bicyclic structures. The 843 cm⁻¹ peak corresponds to the asymmetric oxygen stretch along the Cr-O-Cr framework and is observed in both the bare and ligand coated fused bicyclic and ring structure. The 946, 970, and 1018 cm⁻¹ peaks correspond to a Cr-O stretch. Although not observed in a predicted spectrum, it is not unreasonable to assign these peaks as such. The Cr-O stretch in a fully oxidized chromium complex is known to occur in the 900-950 cm⁻¹ region.¹

Clusters were also probed by surface enhanced Raman spectroscopy (SERS). Standard Raman experiments on the cluster solution did not produce a detectable signal. Therefore, the solution was dried onto a silver nanorod substrate²⁹ for signal enhancement. The experimental SERS spectrum and the predicted spectra for bare clusters are shown in Figure 3.13 and those for the ligand-coated clusters are shown in Figure 3.14 (please refer to the Supporting Information of the published manuscript for spectra of all calculated cluster sizes). As with the UV/Visible and infrared spectroscopy, interpretation and definitive assignment of the spectra is difficult. In addition to the previously mentioned complications, the predicted Raman spectra do not include any corrections for surface enhancement factors. It is known that the surface enhancement process does not increase the intensity of the observed bands equally.⁴⁶⁻⁴⁸ However, reports of Raman spectra collected from chromium oxide nanoparticles have broad bands, similar to our SERS spectrum at 930, 885, 560, and 370 cm⁻¹.^{1-2,49}

In the SERS spectrum, the 360 cm⁻¹ band corresponds to the C=O bending mode, the 570 cm⁻¹ band corresponds to the Cr-O-Cr symmetric stretch. The bands in the 800-900 cm⁻¹ region correspond to the C=O stretch. Again, no one cluster size can be assigned to the experimental spectrum and the spectra predicted for the large open (5,14) clusters most closely match the experimental spectrum rather than those of the small compact structures.

Conclusion

Ultra-small ligand-coated chromium oxide nanoclusters were produced in the LVFR apparatus. The clusters are smaller than other chromium oxide nanomaterials produced previously. Mass spectrometric analysis confirmed prominent cluster stoichiometries of Cr_3O_7 , Cr_4O_{10} , Cr_5O_{14} , and Cr_6O_{14} . However, interpretation of spectroscopic data was more difficult and no one cluster size can be identified. The cluster solution is a complex mixture of cluster sizes and possibly contains multiple isomers or spin states. We are also limited by the DFT calculations and cannot calculate larger structures or those with more than a few ligands. The predicted spectra for the larger more open structures (e.g. Cr_5O_{14} ring) appear to be the best match for our experimental data, especially the SERS and infrared spectroscopy. Preliminary investigations into separation and isolation of the clusters with HPLC has shown multiple

components are present in the solution, but additional experiments and analysis would be needed to isolate cluster sizes and isomers for a more complete characterization to determine the exact composition and ratio of clusters in the sample solution. Further computations on fully ligated clusters are also needed. While the interpretation and definitive assignment of spectroscopic data are difficult, ligand-coated chromium oxide clusters were made and have structures unlike other previous materials.

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Figure 3.1 Laser desorption time of flight mass spectrum. Desorption laser: 532 nm, 1mJ/pulse.



Figure 3.2 LD TOF-MS of material produced at "high", "medium", and "low" laser power. Desorption laser: 532 nm, 0.5 mJ/pulse.



Figure 3.3 Positive mode electrospray ionization time of flight mass spectrum.



Figure 3.4 Simulated isotopic distributions (blue trace) compared to experimental ESI spectra (black trace). Isotope distributions were simulated in Isopro 3.1



Figure 3.5. Lowest energy structures calculated by DFT at the BP86/TZVP level of smaller bare clusters. Relative energies in kcal/mol.



Figure 3.6. Lowest energy structures calculated by DFT at the BP86/TZVP level of larger clusters. Relative energies in kcal/mol.



Figure 3.7. Ligand-coated cluster structures calculated by DFT at the BP86/TZVP level (5,14 clusters are calculated with DZVP).

Table 3.1. Relative energies and ligand binding energies for $Cr_xO_y(MeCN)_z$ clusters. Cluster sizes with Cr_2 to Cr_4 are calculated at the BP86/TZVP level with energies relative to the lowest energy bare cluster. Cr_5O_{14} cluster energies are calculated at the BP86/DZVP level with energies relative to lowest bare isomer structure, comparing the ring, fused-bicyclic, and spiro-bicyclic structures. All energies are corrected for the zero-point vibrational energy.

Cluster	2S+1	Total Energy (hartrees)	Relative Energy (kcal/mol)	Binding Energy (kcal/mol)
MeCN	1	-132.755623 (TZVP)	
MeCN	1	-132.720349 (1	DZVP)	
Cr ₂ O ₂ Ring	1	-2239.756818	+32.5	-
Cr ₂ O ₂ (MeCN) ₃ Ring	1	-2638.128559	-33.3	-
Cr ₂ O ₂ (MeCN) ₄ Ring	1	-2770.941557	-69.3	36.0
Cr ₂ O ₂ Ring	3	-2239.764917	+27.4	-
Cr ₂ O ₂ (MeCN) ₃ Ring	3	-2638.179016	-65.0	-
Cr ₂ O ₂ (MeCN) ₄ Ring	3	-2270.963868	-83.3	18.3
Cr ₂ O ₂ Ring	9	-2239.808616	0.0	-
Cr ₂ O ₂ (MeCN) ₃ Ring	9	-2638.182593	-67.2	-
Cr ₂ O ₂ (MeCN) ₄ Ring	9	-2270.930193	-62.2	-5.0
Cr ₂ O ₄ Ring	1	-2390.424585	+5.1	-
Cr ₂ O ₄ (MeCN) Ring	1	-2523.232626	-27.8	32.9
Cr ₂ O ₄ (MeCN) ₂ Ring	1	-2656.031226	-54.7	27.0
Cr ₂ O ₄ (MeCN) ₃ Ring	1	-2788.769843	-44.1	-10.7
Cr ₂ O ₄ Ring	3	-2390.432766	0.0	-
Cr ₂ O ₄ (MeCN) Ring	3	-2323.232111	-27.4	27.4
Cr ₂ O ₄ (MeCN) ₂ Ring	3	-2656.023566	-49.9	22.5
Cr ₂ O ₄ (MeCN) ₃ Ring	3	-2788.766568	-42.0	-7.9
	1	2661 000602	0.4	
Cr_3O_7 Cage	1	-3661.008603	+8.4	-
$Cr_{3}O_{7}(MeCN)$ Cage	1	-3/93.811/64	-21.5	29.8
$Cr_3O_7(MeCN)_2$ Cage	1	-3926.580978	-30.0	8.5
$Cr_3O_7(MeCN)_3$ Cage	1	-4059.338596	-31.2	1.3
Cr ₃ O ₇ Cage	3	-3661.020522	+0.9	-
$Cr_3O_7(MeCN)$ Cage	3	-3/93.80/136	-18.6	19.4
$Cr_3O_7(MeCN)_2$ Cage	3	-3926.584055	-31.9	13.4
$Cr_3O_7(MeCN)_3$ Cage	3	-4059.349913	-38.3	6.4
Cr ₃ O ₇ Cage	5	-3661.021943	0.0	-
Cr ₃ O ₇ (MeCN) Cage	5	-3/93.807685	-18.9	18.9
$Cr_3O_7(MeCN)_2$ Cage	5	-3926.583535	-31.6	12.7
$Cr_3O_7(MeCN)_3$ Cage	5*	-	-	-

Cr ₄ O ₁₀ Cage	1	-4931.654504	0.0	-
Cr ₄ O ₁₀ (MeCN) Cage	1	-5064.412112	-1.2	1.2
Cr ₄ O ₁₀ (MeCN) ₂ Cage	1**	-5197.167950	-1.4	0.1
Cr ₄ O ₁₀ Cage	3	-4931.629479	+15.7	-
Cr ₄ O ₁₀ (MeCN) Cage	3	-5064.394137	+10.0	5.7
Cr ₄ O ₁₀ (MeCN) ₂ Cage	3**	-5197.149493	+10.2	-0.2
Cr ₅ O ₁₄ Spiro-bicyclic	1	-6276.310160	+12.0	-
Cr ₅ O ₁₄ (MeCN) Spiro	1	-6409.040377	+1.3	6.2
Cr ₅ O ₁₄ (MeCN) ₂ Spiro	1	-6541.763516	-0.2	1.8
Cr5O14 Spiro-bicyclic	3	-6276.319950	+39.8	-
Cr5O14(MeCN) Spiro	3	-6409.057319	+2.3	10.7
Cr ₅ O ₁₄ (MeCN) ₂ Spiro	3	-6541.780116	-0.1	1.5
Cr ₅ O ₁₄ Ring	1	-6276.275660	+27.8	-
Cr ₅ O ₁₄ (MeCN) Ring	1	-6409.055733	-1.8	37.5
Cr5O14(MeCN)2 Ring	1	-6541.779881	-4.1	2.4
Cr5O14 Ring	3	-6276.294707	5.2	-
Cr ₅ O ₁₄ (MeCN) Ring	3	-6409.062211	-13.9	29.6
Cr ₅ O ₁₄ (MeCN) ₂ Ring	3	-6541.786317	-15.0	2.4
Cr ₅ O ₁₄ Fused-bicyclic	:1	-6276.330763	5.2	-
Cr ₅ O ₁₄ (MeCN) Fused	1	-6409.08158	-13.9	19.1
Cr ₅ O ₁₄ (MeCN) ₂ Fused	11	-6541.803724	-15.0	1.1
Cr ₅ O ₁₄ Fused-bicyclic	:3	-6276.339057	0.0	-
Cr ₅ O ₁₄ (MeCN) Fused	3	-6409.076000	-10.4	10.4
Cr ₅ O ₁₄ (MeCN) ₂ Fused	13	-6541.800331	-12.9	2.5

* Theory calculations for Cr_3O_7 (MeCN)₃ in the quintet spin state do not result in a local minimum, therefore, binding energies cannot be calculated for this spin state. ** The Cr_4O_{10} (MeCN)₂ Cage singlet and triplet states have imaginary frequencies resulting from the methyl group rotation on acetonitrile.



Figure 3.8. UV/Visible absorption (blue trace) spectrum of $Cr_xO_y(MeCN)_z$ clusters. Comparison to L.S. Wang PES experiment transitions shown in purple for (2,4) clusters and green for (4,10) clusters.¹⁶ Emission spectrum (red trace) from excitation at 355 nm.



Figure 3.9. UV/Visible absorption spectrum compared to predicted TD-DFT spectra for large bare clusters.



Figure 3.10. UV/Visible absorption spectrum compared to predicted TD-DFT spectra for large ligand-coated clusters.



Figure 3.11. Infrared spectrum compared to the predicted spectra of large bare clusters.



Figure 3.12. Infrared spectrum compared to the predicted spectra of large ligand-coated clusters.



Figure 3.13. Surface enhanced Raman spectrum (SERS) compared to the predicted spectra of large bare clusters.



Figure 3.14. Surface enhanced Raman spectrum (SERS) compared to the predicted spectra of large ligand-coated clusters.

CHAPTER 4

LASER SYNTHESIS OF MOLYBDENUM OXIDE NANORODS

Introduction

Molybdenum oxide nanoparticles are of great interest due to their catalytic,¹⁻⁴ electrochemical,^{1,5-10} and photochromic properties.¹¹⁻¹⁶ Molybdenum oxide particles have recently been used in biological applications to provide antimicrobial material coating¹⁷⁻¹⁸ and disease treatment alternatives.¹⁹⁻²¹ Hydrothermal or solvothermal reactions^{1-2,6,10,20,22-} 24 are the typical methods for synthesis of molybdenum oxide nanoparticles but they can also be synthesized by wet chemical reduction reactions,^{21,25-26} sol-gel methods,^{5,27} sonication,²⁸⁻³⁰ electrochemical reactions,^{3,16,18} vapor deposition methods,^{8,14,31} as well as laser-based techniques.^{11-12,15,32-33} These methods can produce a wide variety of morphologies ranging from an irregular shape to uniformly shaped spheres, rods, prisms, or other nanostructures. Some methods produce discrete particles while others produce thin films on substrates. Typically, these materials are between several hundred nanometers and many microns in size. Here we report a laser vaporization flow reactor (LVFR) synthesis method that produces molybdenum oxide nanorods grown in the gas phase, coated with acetonitrile, and then condensed in a liquid nitrogen cold trap. These colloidal nanorods on the nanometer size scale are smaller than other rods presented in the literature synthesized by other methods.
Experimental

The laser vaporization flow reactor has been previously described³⁴⁻³⁷ and has been used to synthesize smaller molecular-sized ligand-coated nanoclusters^{34-35,37} or larger ligand-coated nanoparticles.³⁶ In brief, a molybdenum rod was ablated with a 248 nm high power (100-140 mJ/pulse), high repetition rate (300-400 Hz) excimer laser (Coherent LPX Pro 240F, KrF) focused to a spot size of 3x10 mm under a flow of 10% O₂ in helium. The pressure in the flow tube was maintained at 10 torr. Ligands were added downstream of the vaporization point by heating acetonitrile to 50 °C and entraining the vapor into an argon flow. After ligand addition, the gas mixture flowed into and was condensed in a liquid nitrogen cold trap. Sample collection occurs over a period of four hours. Excess ligand was added, then the frozen trapped material was removed from the trap and warmed to room temperature under an argon flow. After warming, a clear to blue solution was obtained for analysis. In exploring various experimental conditions, we find laser power and percentage of oxygen to be the most important parameters in producing nanorods. Ablation pulse energies below 100 mJ did not produce a significant amount of material, whereas higher pulse energies (150 mJ and higher) did not produce rods but more irregular spherical shaped particles in solution. In addition to the nanoparticles, a large amount of light blue material was deposited on the walls of the apparatus and not entrained in the gas flow and therefore not ligand coated. Because the material is not ligand-coated, it is insoluble. This material was removed from the wall for analysis and is consistent with bulk MoO₃. Experiments with 1% and 5% oxygen result in nanoparticles not nanorods.

We investigated particle morphology, size, and distribution by transmission electron microscopy (TEM) (FEI Tecnai 20, 200 kV) imaging and ImageJ software.³⁸ Elemental composition was obtained by scanning transmission electron microscopy with an energy dispersive x-ray spectroscopy detector (STEM-EDS) (FEI Teneo). Optical absorption and emission were explored with UV/Visible (Shimadzu UV-2600) and fluorescence spectroscopy (Shimadzu RF-5301C). Infrared (Nicolet 6700 FT-IR; diamond ATR accessory) and Raman spectroscopy (Thermo DXR Raman Microscope) were employed for further material characterization. The catalytic activity of the rods was tested by spectroscopically monitoring the degradation of methylene blue.⁴

Results and Discussion

Medium Laser Power Nanorods

Analysis of the molybdenum oxide solution by laser desorption and electrospray ionization mass spectrometry did not indicate the presence of small molecular sized nanoclusters (further details of mass spectrometry experiments are discussed in Chapter 5). Therefore, electron microscopy was employed to investigate the presence of larger nanoparticles. Imaging of the particles revealed nanorods roughly 100 x 20 nm in size, as shown in the TEM image in Figure 4.1. Particle size analysis (Figure 4.2) of 217 rods measured in Image J software³⁸ indicate an average length of 89 nm and width of 22 nm, resulting in an average aspect ratio (length/width) around 4. Imaging fresh and aged (up to a month) samples resulted in similarly shaped and sized rods, indicating that the growth of the nanoparticles occurs during the LVFR synthesis and not post-synthesis. Nanorods produced by previously mentioned hydrothermal synthesis, vapor deposition, or sol-gel methods have a different morphology compared to the rods produced by the LVFR method. These rods can be up to several microns long and hundreds of nanometers wide. Saupe and coworkers²⁵ and Ferrer and coworkers²⁶ report an aspect ratio of 60 for their nanorods, compared to our LVFR synthesized nanorods with an aspect ratio of 4. Other laser based synthesis methods produce irregularly shaped nanomaterial^{11,15} or films³² that differ from the nanorods produced by here. Elemental composition from STEM-EDS analysis confirmed the presence of molybdenum and oxygen. The crystal structure of the material was investigated with high resolution TEM and electron diffraction; however, the rods appeared to be unstable under more intense electron beams. Any observed lattice spacings or diffraction spots appeared to be induced by interaction with the electron beam. Diez-Drougett et al. have studied the structural effects of electron beam irradiation on amorphous³⁹ and crystalline⁴⁰ molybdenum oxide materials. When studying amorphous molybdenum oxide, they observed a shift from an amorphous to crystalline structure with increased electron beam exposure. XRD analysis of drop casted material was inconclusive due to the lack of material available even when multiple runs were combined.

The optical properties of the molybdenum oxide solution were investigated with UV/Visible and fluorescence spectroscopy. The blue color of the solution is common among molybdenum oxide materials and is attributed to the Mo⁺⁵ oxidation state, where fully oxidized materials, in the +6 oxidation state, are white.¹³ Figure 4.3 shows the UV/Visible absorption spectrum (black trace) of the molybdenum oxide solution with absorption peaks observed at 315 nm and 215 nm. There is a low intensity broad absorption throughout the visible region that is not obvious until compared to the baseline

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acetonitrile measurement (blue trace, inset Figure 4.3). Our UV/Visible spectrum is in good agreement with spectra produced by Cao and coworkers²³ of their hydrothermally synthesized nanoprisms and nanobelts, which are up to 330 nm wide, 90 nm thick, and up to 10 microns long. They report the band gap, derived from a Tauc plot, for their nanobelts to be 2.82 eV and for their nanoprisms to be 3.64 eV. Using a similar Tauc plot of our absorption spectra (Figure 4.4), we derive a band gap of 3.48 eV for our material. More recently, Saupe and coworkers²⁵ synthesized *h*-MoO₃ hexagonal rods with aspect ratios of 60 through wet chemical reduction reactions. For their rods, they report the onset of absorption at 411 nm with a band gap of 3.017 eV. Our nanorods therefore have absorption profiles and band gaps comparable to those of other molybdenum oxide nanomaterials.

Optical emission of the particles was explored by fluorescence spectroscopy with excitation throughout the UV region ranging from 220 nm (instrument lower limit) to 400 nm as shown in Figure 4.5. Emission spectra were collected starting 10 nm from the excitation wavelength and ending 10 nm before the second order diffraction peak to eliminate signals attributed to the excitation source. Excitations from 220-300 nm produce an emission peak in the 250-350 nm range with a λ_{max} around 290nm and excitations from 275-400 nm produce a broad emission peak in the 450-550 nm range with a λ_{max} around 480 nm. A pure sample of acetonitrile excited under the same conditions has an emission band around 310 nm (Figure 4.6). No background subtractions or corrections were applied to the fluorescence spectrum shown in Figure 4.5. Pillai and coworkers³¹ have grown molybdenum oxide nanorods onto substrates by RF magnetron sputtering followed by annealing at various temperatures. They report a

broad photoluminescence from 345-556 nm, when the sample was excited at 250 nm, with structure that varied with annealing temperature. Zhang and coworkers⁴¹ have synthesized quantum dots that emit at 400 nm when excited at 300 nm.

In addition to the electronic spectroscopy, the vibrational spectra of the molybdenum oxide sample were explored with infrared and Raman Spectroscopy. The infrared spectrum was measured via attenuated total reflectance (ATR) by drying the sample under ambient conditions and placing the resulting solid onto the diamond ATR crystal (Figure 4.7, top trace). The sample spectrum was compared to pure acetonitrile (bottom trace) and a commercial MoO₃ powder. The peaks observed at 3161 cm⁻¹ and 1633 cm⁻¹ can be attributed to adsorbed water. No precautions were taken to avoid the adsorption of ambient water. The peaks at 2261, 1428, and 1040 cm⁻¹ indicate the presence of acetonitrile. The C-N stretch is shifted 9 cm⁻¹ from the liquid phase value indicating that acetonitrile is bound to the surface of the particles. Peaks attributed to molybdenum oxide stretches occur at 946 cm⁻¹ and 896 cm⁻¹. A commercial MoO₃ nanopowder obtained from Sigma-Aldrich, analyzed under the same conditions as our sample, has peaks at 978, 849, and 812 cm⁻¹. Cao and coworkers²³ reported an infrared spectrum of their rods and assigned the band at 995 cm⁻¹ to the terminal Mo=O stretch and the bands at 874 and 555 cm⁻¹ to Mo-O-Mo bends, consistent with MoO₃. Zhou and coworkers⁴² report a Mo=O band at 925 cm⁻¹ for their MoO₂ nanomaterials. The infrared spectrum indicates that our material is consistent with other MoO₃ materials with acetonitrile ligands bound to the surface.

The Raman spectrum of the sample was collected by drying the sample under ambient conditions into a thin film onto a glass slide which was excited at 780 nm. The spectrum was compared to a commercial MoO₃ powder shown in Figure 4.8. The commercial powder (bottom trace, Figure 4.8) has a peak at 993 cm⁻¹ corresponding to the Mo=O terminal stretch while peaks at 817 and 664 cm⁻¹ correspond to the Mo-O bridging stretches. In our sample, we observe broad peaks consistent with amorphous molybdenum oxide^{13,33,43} with low laser power and acquisition times (less than 4 mW/100 sec exposure, 1 micron spot) (top trace, Figure 4.8). We also observe spectral changes with increased laser power and irradiation times (up to 8 mW/200 sec exposure, 1 micron spot) during Raman analysis. With higher laser power and irradiation time, sharps peaks would grow in on top of the broad peaks initially observed. This is consistent with other studies of laser induced structural changes in molybdenum oxide materials. Amorphous molybdenum oxide is known to crystalize under laser induced annealing, as shown in experiments by Gong and Haur³³ and Camacho-Lopez and coworkers.⁴³⁻⁴⁴

To further investigate the crystallization of our material, the Raman sample was annealed in air at 400 °C for 1 hour (ramp rate of 10°C/min) similar to the conditions used by Pillai and coworkers ³¹ and Sian and Reddy.⁴⁵ After annealing, the sample was reanalyzed under the same conditions. When viewing the sample under the Raman microscope, there was an obvious visual change from blue to white material in portions of the annealed sample. Spectra collected from the white areas contained prominent peaks at 994, 817, and 665 cm⁻¹ consistent with MoO₃ (middle trace, Figure 4.8). This is consistent with the blue color coming from the molybdenum in the +5 oxidation state and upon annealing in air becoming more fully oxidized, producing white material with molybdenum in the +6 oxidation state. Hu and coworkers²⁰ report a Raman spectrum for their nanomaterials and assigned the 994 cm⁻¹ band to the Mo=O stretch, the 810 cm⁻¹ band to the Mo₂-O bridge, and the 655 cm⁻¹ band to the Mo₃-O bridge. Chu and coworkers³⁰ reported Raman spectra of α -MoO₃·H₂O with bands at 969, 926, 697, 393, 239, 199, 171, 144, and 125 cm⁻¹ that are consistent with hydrated molybdenum oxides. Sunkara and coworkers⁸ reported Mo-O stretching at 905 cm⁻¹ and 984 cm⁻¹, Mo-O₂ stretching at 830 cm⁻¹, and Mo-O₃ stretching at 799 cm⁻¹ for their nanowire arrays. Raman analysis indicates the material as produced is amorphous and can crystalize upon annealing.

Investigation into the catalytic activity of our materials was done by monitoring the degradation of a methylene blue solution, as described previously by others in the literature.^{4,46-47} The dried molybdenum oxide sample was added to a methylene blue aqueous solution (10 mg/L) in a ratio of 1 mg catalyst to 2 ml solution. The solution was stirred in the dark for 30 minutes before irradiation with UV light (Spectroline ENF-260C, 365 nm) to allow for an adsorption/desorption equilibrium to be established. Aliquots were taken from the reaction flask every 30 minutes and the UV/Visible absorption spectrum was monitored for 180 minutes. The "0 min" spectrum was collected after the 30 minutes of stirring in the dark but before irradiation of UV light. The catalytic activity of the sample was compared to a blank methylene blue solution without catalyst (Figure 4.9) and to a commercial MoO₃ powder (Figure 4.10). The blank solution absorbance spectrum did not change throughout the experiment. The commercial sample degraded the methylene blue. As the methylene blue is degraded, the solution was visually observed to change from blue to clear and characteristic peaks in the UV/Vis spectrum at 665, 615, and 290 nm decreased overtime and the peak at 210 nm increased.

Unlike the commercial material, with our dried molybdenum oxide material, the methylene blue solution turned from a bright blue to a darker blue/purple almost instantaneously when the dried material was added. The initial absorption spectrum of the methylene blue solution had much broader and weaker peaks compared to the blank or commercial sample, which is reasonable given the initial color change upon mixing. The absorption peaks in the 600 nm region of the spectrum decreased over time and the solution became clear. Considering the immediate color change that occurs upon mixing with our nanorods, compared to the commercial MoO₃ powder, our nanorods appear to be a more active catalyst under the experimental conditions used. An approximate first order kinetic plot, as shown in Figure 4.11, was made to determine the rate constant of the commercial material compared to our molybdenum oxide material. Our material appears to degrade methylene blue two times faster than the commercial sample.

The catalytic reaction also occurred in the dark without UV irritation. The reaction was not spectroscopically monitored, but the color change was visually observed over time. The catalytic test was also performed on a sample of our material after annealing. We observed the same immediate color change as the amorphous material, but the reaction did not seem to progress with time. We attribute this to not fully annealing the sample, where the remaining amorphous material is responsible for the initial reaction, but the crystalline material slowed the reaction progress. Further kinetic testing with more appropriate equipment is needed to quantitatively measure the initial reaction upon mixing our material into the methylene blue solution.

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High Laser Power Material from Apparatus Walls

The high laser power experiments do not produce the nanorods previously discussed. The material captured in solution was irregular shaped globules as shown in the TEM image in Figure 4.12. The material deposited on the walls of the apparatus was scraped off to form a powder shown in Figure 4.13. The powder was analyzed and compared to a commercial MoO₃ powder. The powder is consistent with amorphous MoO₃, as shown by the XRD pattern and Raman spectrum in Figure 4.14 and Figure 4.15. The powder is insoluble in acetonitrile which makes sense because it does not get entrained in the gas flow and ligand-coated. The catalytic test of this material showed the initial color change from blue to purple that was observed in the ligand-coated nanorod material, however, the reaction did not progress past this point.

Conclusion

The laser vaporization flow reactor synthesis method was used to make colloidal molybdenum oxide nanorods with an aspect ratio of 4. These colloidal particles appear to have a much smaller and uniform size, different from those molybdenum oxide nanorods produced by other methods, which can be microns in length and have aspect ratios as high as 60.²⁵⁻²⁶ The molybdenum oxide sample solution does not appear to be air sensitive and is shelf stable over extended periods of time (several months). The solvent can be dried off, leaving behind a blue film which can be redispersed in acetonitrile, as well as other polar organic solvents. The nanorods appear to be amorphous based on the material behavior during Raman analysis and TEM imaging. The optical properties and

catalytic activity of these nanorods were measured and are comparable to other experimental results reported in literature.

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Figure 4.1. Transmission electron microscopy (TEM) image of $Mo_xO_y(MeCN)_z$ material. Particle size analysis indicates rods roughly 100 x 20 nm. Scale bar 100 nm.



0 -

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Number of Particles: 217 Average Length: 89 nm Average Width: 22 nm Average Aspect Ratio: 4

50

100

Length (nm)

150

200

Figure 4.2. Particle size analysis of rods from several TEM images.

20 22 24 26 28 30 32

Width (nm)

0 | 10

12 14 16 18



Figure 4.3. UV/Visible absorbance spectra of $Mo_xO_y(MeCN)_z$ solution (black trace) and acetonitrile baseline (blue trace). Inset shows the low intensity broad absorption throughout the visible region.



Figure 4.4. Tauc plot of UV/Visible absorption spectrum to determine the band gap of 3.48 eV.



Figure 4.5. Emission spectra of $Mo_xO_y(MeCN)_z$ solution at various excitation wavelengths.



Figure 4.6. Emission spectra of neat acetonitrile at various excitation wavelengths.



Figure 4.7. Attenuated total reflectance infrared spectrum of the dried $Mo_xO_y(MeCN)_z$ material and neat acetonitrile. The peak at 2261 cm⁻¹ indicates that there is acetonitrile bound to the surface of the nanorods.



Figure 4.8. Raman spectrum of dried $Mo_xO_y(MeCN)_z$ material (top trace) compared to the spectrum of the dried $Mo_xO_y(MeCN)_z$ material after annealing for 1 hour at 400 °C (middle trace) and a commercial MoO_3 powder (bottom trace). The $Mo_xO_y(MeCN)_z$ material spectrum is consistent with amorphous molybdenum oxide that can be crystalized upon annealing.



Figure 4.9. Absorption spectra of the blank methylene blue solution under UV radiation. The UV light did not degrade the methylene blue solution without the presence of a catalyst.



Figure 4.10. The left panel shows the absorption spectra for the catalytic reaction of the commercial powder. The right panel shows the absorption spectra for the catalytic reaction of the dried $Mo_xO_y(MeCN)_z$ material.



Figure 4.11. First order kinetic plot of integrated area of UV/Visible absorption peaks as a function of time.



Figure 4.12. TEM images of particles from solution of high laser power sample. Scale bar is 50 nm. (JEOL JEM 1101 80kV)



Figure 4.13. Photograph of solid material (12 mg) collected from the walls of the LVFR apparatus.



Figure 4.14. The solid powder appears to be amorphous as shown by the XRD analysis (Bruker D8 Advance Co K α λ =1.7890Å, zero background silicon wafer, 0.6 scan speed, 30 min scan) of the solid material with background subtraction (top trace) compared to the commercial MoO3 powder (middle trace) and a library reference pattern, JCPDS # 00-035-609 (bottom trace).



Figure 4.15. Raman spectrum of scraped powder consistent with amorphous MoO₃ (Renishaw inVia Microscope, 785 nm).

CHAPTER 5

STABLE POLYOXOANION CLUSTERS PRODUCED VIA NANOROD SPUTTERING IN AN ELECTROSPRAY MASS SPECTROMETER

Introduction

Electrospray ionization mass spectrometry (ESI-MS) has generally been regarded as a gentle ionization method for analysis of molecules in solution with little fragmentation observed compared to other ionization techniques.¹⁻³ Because little fragmentation is observed during analysis, ESI-MS is widely used for biological and organic molecules,⁴⁻⁵ but it has also been used to study inorganic molecules and metal clusters.⁶⁻⁹ However, some studies have shown the destructive nature of the electrospray ionization process by varying cone voltages of the spectrometer.¹⁰⁻¹¹ In electrospray ionization, fragmentation can occur between the spray tip and the cone of the mass spectrometer.³ Landridge-Smith and coworkers have shown the loss of ligands in a rhodium carbonyl complex with an increase in cone voltage.¹⁰ Zhang and Schwarz have shown that vanadium oxide clusters of various stoichiometries can be produced from a vanadyl isopropoxide solution in an ESI-MS with varying cone voltages.¹¹ Yu and coworkers observed fragmentation in their ESI spectrum of CdTe intermediates during synthesis of CdTe quantum dots.¹² Previously we have studied ultra-small ligand-coated chromium oxide nanoclusters by both laser desorption ionization (LD) and ESI mass spectrometry.¹³ We observed more fragmentation and loss of ligands from the $Cr_xO_v(MeCN)_z$ clusters in the ESI spectrum compared to the laser desorption ionization

spectrum. Here we report the production of polyoxomolybdate anions by sputtering of ligand-coated molybdenum oxide nanorods within an ESI mass spectrometer.

These molybdenum oxide nanorods fall under the larger class of compounds, polyoxometalates, which includes heteropolyoxometalates and polyoxoanions with a wide variety of compositions and structures.¹⁴⁻¹⁵ Here we focus only on iso-polyoxoanion molybdates. Polyoxoanion molybdates have been previously observed by electrospray ionization mass spectrometry;¹⁶⁻¹⁹ these experiments used a solution of the polyoxoanion salt of interest and observed fragmentation of the parent ion under various spectrometer conditions. We have observed formation of stable clusters of molybdenum polyoxoanions from nanorods in an electrospray time-of-flight mass spectrometer. To our knowledge, stable polyoxoanions produced by sputtering from larger nanoparticles in an electrospray source have not been reported in the literature.

Experimental

Nanorod Synthesis

Detailed discussion on the synthesis and characterization of the molybdenum oxide nanorods was discussed in Chapter 4. In brief, a molybdenum rod is vaporized under a flow of oxygen, coated with acetonitrile ligands, and condensed in a liquid nitrogen cold trap. The frozen material was then warmed to room temperature providing a solution of ligand-coated molybdenum oxide material for analysis.

Mass Spectrometry

Neat LD-TOF and MALDI were used to analyze the experimental material and a commercial MoO₃ powder. The commercial powder was suspended in acetonitrile then dropped and dried onto the sample probe tip for neat desorption. Neat desorption of the synthesized material was unsuccessful, therefore, the MALDI matrix 2,5dihydroxybenzoic acid (DHB) was utilized. Spectra of the Mo_xO_y(MeCN)_z material were collected in both positive and negative mode. The 3rd harmonic (355 nm) of an Nd:YAG laser (New Wave Research Polaris II) with 1 mJ/pulse or lower was used for desorption.

Electrospray negative ion spectra were collected on a Mariner PerSeptive Biosystems mass spectrometer from 50-2000 m/z. The molybdenum oxide/acetonitrile solution was injected, as synthesized, directly into the instrument via syringe pump with a flow rate of 20 μ l/min with nitrogen as the desolvation and nebulization gas. The spray tip voltage was set to 3500 V and the cone voltage was varied from a low to high voltage (50-200 V) to investigate fragmentation of the sample while all other instrument parameters were held constant throughout the experiment once adjustments for optimal signal detection were made.

Results and Discussion

Mass spectrometry experiments were used to determine the presence and stoichiometries of small nanoclusters present in the $Mo_xO_y(MeCN)_z$ solution. Laser desorption time of flight mass spectra were difficult to obtain. Neat laser desorption of the material did not result in a spectrum containing molybdenum oxide. While still difficult, using the MALDI matrix DHB did help with the desorption of the sample. The positive mode and negative mode spectra are found in Figure 5.1 and 5.2, respectively. However, due to the large number of molybdenum isotopes, presence of matrix, and the mass resolution of the MALDI data, it is difficult to make mass assignments. In the positive spectrum (Figure 5.1), we observed a peak spacing of 144 amu which is consistent with MoO₃. The only peak in the negative spectrum (Figure 5.2) that is not attributed to the matrix material is the peak at m/z= 403 which does not appear to contain molybdenum oxide. Several groups report prominent clusters of Mo_xO_y of (2,4), (3,8), (4,10), and (5,14) in their mass spectra of molybdenum oxide.²⁰⁻²²

These difficulties in obtaining a laser desorption mass spectrum suggested that large nanoparticles were present and not smaller molecular clusters. Our group has previously established the capability of LD-TOF-MS to detect small molecular sized ligand-coated clusters.^{13,23} Thin layer chromatography analysis was also performed to separate and identify multiple cluster sizes. Several solvent systems were tried and the Mo_xO_y(MeCN)_z sample did not move off the baseline, further supporting the idea that large nanoparticles were present in solution and not small nanoclusters. Transmission electron microscopy (TEM) was used to image the nanorods which were found to be 100 x 20 nm in size, as shown in Figure 5.3. Nanorods with such high mass would not be detectable on our LD-TOF-MS instruments.

Electrospray ionization mass spectrometry was much more successful and resulted in more consistent data compared to LD-TOF MS. ESI spectra were collected in both positive ion and negative ion mode. There were no molybdenum oxide peaks observed in the positive ion mode spectra. However, molybdenum oxide peaks were observed in the negative ion mode spectra. The top spectrum in Figure 5.4 shows a

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spectrum collected with a 50 V cone voltage. Peak assignments are made based on isotopic distributions and spacings, and comparisons to simulated distributions calculated in the Isopro 3.1 software program.²⁴ The most prominent peak appears at m/z= 440 with smaller peaks at m/z= 408, 608, 696, and 912. The peak spacing within the isotopic distribution of the m/z= 440 peak indicates a doubly charged species which corresponds to $[Mo_6O_{19}]^{2-}$. This was confirmed by simulated isotopic distributions which are shown in the bottom spectrum of Figure 5.4. We have not observed doubly charged ions under similar instrument conditions in previous experiments.¹³ Molybdenum has seven naturally occurring isotopes which combined with low signal to noise makes assignments of the other peaks in the spectrum more difficult. Possible mass assignments are listed in Table 5.1.

The cone voltage was increased to study fragmentation as a function of cone voltage. One would typically expect an increase in low mass fragments as the voltage is increased, however, when the voltage was increased to 100 V we also observed an increase in higher mass fragments as shown in Figure 5.5. We observed a series of peaks separated by 72 mass units with again the most prominent peak at m/z= 440. Low mass fragments at m/z= 369, 297, and 224 were observed and are in agreement with the fragments observed by Poblet and coworkers in their study of tertbutyl ammonium hexamolybdate ((*n*-C₄H₉)₄N)₂Mo₆O₁₉.¹⁹ These peaks have isotopic distribution spacings of doubly charged ions which correlate to $[Mo_5O_{16}]^{2-}$, $[Mo_4O_{13}]^{2-}$, and $[Mo_3O_{10}]^{2-}$ respectively.

In addition to these low mass fragments we also observe an increase in higher mass fragments, up to m/z=872, as shown in Figure 5.5. Due to the low signal to noise of

peaks m/z= 584 and higher, it is difficult to make mass assignments confidently. Peaks from 224-512 have enough signal intensity to confirm the isotopic distribution spacing of a doubly charged ion. However, the higher mass peaks have low signal intensity and spacings cannot be confirmed, therefore these mass assignments are given with lower confidence. There may be other possible mass assignments from singly charged ions. For example, the peak at m/z=728 [10,31,0]²⁻ could also be assigned to m/z=729 [5,13,1]⁻, Triply charged ions were not considered and may be a possibility as well. Other possible mass assignments can be found in Table 5.2 with the most likely clusters shown in bold.

The most logical peak assignments (bold in Table 5.2) correspond to cluster sizes with increasing MoO₃ units, which is the stable form of molybdenum oxide found in nature. This is indicated by the peak spacings of 72 mass units, corresponding to a doubly charged MoO₃. Our group has also studied molybdenum oxide cluster cations in multiphoton photodissociation mass spectrometry experiments.²⁵ The mass spectrum contained peaks with stoichiometries similar to those observed in our ESI spectrum. Photofragmentation of the clusters indicated loss of MoO₃ and excess oxygen.

Conclusion

Mass analysis of molybdenum oxide nanorods has demonstrated the destructive behavior of electrospray mass spectrometry. We observed stable polyoxoanions produced by sputtering of molybdenum oxide nanorods in an electrospray source. The polyoxoanions produced are consistent with other polyoxoanion molybdates produced in previous reports. As the cone voltage is increased, the cluster sizes observed increased and differed by MoO₃ units.
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Figure 5.1. Positive mode LD-TOF-MS. Reference commercial MoO_3 powder sample suspended in acetonitrile and dried onto sample probe tip (top trace) compared to $Mo_xO_y(MeCN)_z$ MALDI spectrum (bottom trace). Red dash lines indicate peaks present in both the MoO₃ reference spectrum and the $Mo_xO_y(MeCN)_z$ spectrum.



Figure 5.2. Negative mode LD-TOF MS of $Mo_xO_y(MeCN)_z$ MALDI spectrum (bottom trace) compared to a blank DHB spectrum (top trace). Red dash lines indicate peaks present in both the DHB reference spectrum and the $Mo_xO_y(MeCN)_z$ spectrum.



Figure 5.3. TEM image displaying nanorods roughly 100 x 20 nm. Scale bar 100 nm.



Figure 5.4. Top trace is ESI-MS with cone voltage of 50 V. Bottom trace shows the m/z=440 peak overlaid with a simulated isotopic distribution of $[Mo_6O_{19}]^{2-}$ (blue trace) calculated in Isopro 3.1.

Table 5.1. Possible cluster assignments for 50 V negative mode ESI TOF-MS shown in Figure 5.4. Only masses with up to Mo_{15} , O_{40} , and $MeCN_{15}$ singly or doubly charged were calculated and there may be possible assignments of even larger clusters or higher charged clusters that were not considered. There are possible mass assignments other than those listed below but have been eliminated based on comparison to simulated isotope spectra produced using the Isopro 3.1 program. Most likely cluster size shown in bold.

Peak (m/z)	Cluster Size [Mo, O, MeCN] ⁿ⁻
408	[4,27,0] ²⁻ [5,21,0] ²⁻ [6,15,0] ²⁻
440	[5,25,0] ²⁻ [6,19,0]²⁻ [7,13,0] ²⁻
480	$[3,12,0]^{-}$ $[4,36,0]^{2-}$ $[5,30,0]^{2-}$ $[6,24,0]^{2-}$
481	$[6,19,2]^{2}$
608	[3,20,0] ⁻ [4,14,0] ⁻ [5,8,0] ⁻
912	[4,33,0] ⁻ [5,27,0] ⁻ [6,21,0] ⁻ [7,15,0] ⁻



Figure 5.5. ESI-MS with cone voltage of 100 V. Peaks A-E have isotopic distribution spacings consistent with doubly charged ions while the spacing in peaks F-J cannot be determined due to low signal to noise. Peak assignments are found in Table 5.2.

Table 5.2. Possible cluster assignments for 100 V negative mode ESI TOF-MS shown in Figure 5.5. Only masses with up to Mo_{15} , O_{40} , and $MeCN_{15}$ singly or doubly charged were calculated and there may be possible assignments of even larger clusters or higher charged clusters that were not considered. There are possible mass assignments other than those listed below but have been eliminated based on comparison to simulated isotope distributions produced using the Isopro 3.1 program. Most likely cluster size shown in bold.

Peak Label	Peak (m/z)	Cluster Size [Mo, O, MeCN] ⁿ⁻	
A	224	[2,2,0] ⁻ [3,10,0] ²⁻	
	225	$[2,11,2]^{2-}$ $[3,5,2]^{2-}$	
В	296	[4,13,0]²⁻ [5,7,0] ²⁻ [6,1,0] ²⁻	
	297	$[4,8,2]^{2-}$ $[5,2,2]^{2-}$	
С	368	[5,16,0]²⁻ [6,10,0] ²⁻ [7,4,0] ²⁻	
	369	$[4,17,2]^{2-}$ $[5,11,2]^{2-}$	
D	440	[5,25,0] ²⁻ [6,19,0] ²⁻ [7,13,0] ²⁻	
Е	512	[6,28,0] ²⁻ [7,22,0] ²⁻ [8,16,0] ²⁻	
	513	$[5,29,2]^{2-}$	

Peak Label	Peak (m/z)	Cluster Size [Mo, O, MeCN] ⁿ⁻
F	584	[8,25,0] ²⁻ [9,19,0] ²⁻ [10,13,0] ²⁻
	585	$[2,22,1]^{-}$ $[3,16,1]^{-}$ $[4,10,1]^{-}$ $[5,4,1]^{-}$
G	656	[9,28,0] ²⁻
	657	$[8,29,2]^{2-}$ $[9,23,2]^{2-}$
Н	728	[10,31,0] ²⁻
	729	$[4,19,1]^{-}$ $[5,13,1]^{-}$ $[6,7,1]^{-}$
Ι	800	[6,14,0] ⁻ [7,8,0] ⁻ [11,34,0]²⁻
J	872	[12,37,0] ²⁻

CHAPTER 6

STATUS REPORT ON OTHER SYSTEMS STUDIED

Introduction

The LVFR synthesis method has been used to explore many other systems in addition to the chromium oxide and molybdenum oxide materials discussed in the previous chapters. While some systems like chromium oxide are relatively easy and efficient to synthesize, others are more inefficient, inconsistent in reproducibility, or completely unsuccessful. A full survey of potential systems appropriate for LVFR synthesis is needed. Interesting gas phase clusters outside of metal oxides that have been or would like to be explored in the LFVR apparatus are pure metals, metal carbides (metcars), metal silicon, and metal PAH complexes. The partial work on some of these systems will discussed here.

Metal clusters have shown increased stability that was found to be the result of their interesting electronic and geometric structures. Electronic structures of these metal clusters follow the jellium model,¹ where the valence electrons of each atom add together to complete the orbital shell. Geometric structures follow those described as MacKay icosahedra.² For example, in the mass spectrum of sodium clusters, a high abundance of clusters with 8, 20, 40, 58, and 92 atoms were observed which correspond to the 1p, 2s, 2p, 1g, and 1h shell closings, respectively.³ The aluminum the ion, Al₁₃⁻ was found to be

particularly stable, follow the jellium model and should have a MacKay icosahedra structure.⁴⁻⁷

Metal carbides are some of the hardest bulk materials available, making them an interesting system to study. These metal carbides or "met-cars" were first discovered in the gas phase by Castleman and coworkers in 1992, where they observed the stoichiometry $M_8C_{12}^+$ for titanium, vanadium, zirconium, and halfnium.⁸⁻⁹ Our group studied metal carbide systems with photodissociation experiments and observed the $M_8C_{12}^+$ cluster but also the larger $M_{14}C_{13}^+$ cluster. The structures of these were investigated and the $M_{14}C_{13}^+$ cluster was found to have the "3x3x3" rock salt structure, but the structure of the $M_8C_{12}^+$ is more difficult to determine. A few cage structures were proposed.¹⁰⁻¹²

Metal silicon clusters were first discovered in the gas phase by Beck in 1987, where a high abundance of MSi_{15} and MSi_{16} were observed in the mass spectra.¹³⁻¹⁴ The structure and stability of gas-phase metal silicon nanoclusters have been studied both experimentally¹⁵⁻¹⁷ and theoretically.¹⁸⁻²⁰ It has been found that in MSi_n clusters with $n\leq 12$ the metal is on the surface of the cluster and for $n\geq 13$ the metal is fully encapsulated by silicon atoms.²⁰ Encapsulation eliminates dangling bonds and stabilizes the cluster. Increased abundance of the MSi_{16} clusters has been attributed to both electronic and geometric shell closure.^{17,19}

Nakajima and coworkers investigated the structure and stability of MSi_n clusters with absorption reactivity and anion photoelectron spectroscopy (PES).¹⁷ The reactivity between the clusters and water vapor provided information on the location of the metal atom. The reactivity of silicon is lower than that of a metal, so if the cluster shows high reactivity the metal is likely on the surface, and when the cluster shows low reactivity, the metal is probably encapsulated. MSi_{16} clusters showed no reactivity towards water vapor suggesting that the metal is enclosed in a silicon cage.

Our group used photodissociation experiments to determine metal location in relation to the size of the clusters for copper-, silver-, and chromium-silicon clusters.¹⁶ Copper and silver produced smaller clusters (MSi_{10}^+ and MSi_7^+) while the chromium produced clusters of n=15 and 16 in addition to smaller clusters. Fragmentation of the copper and silver clusters showed loss of the metal while fragmentation of the $CrSi_{15}^+$ clusters showed the loss of silicon. The loss of metal from the smaller clusters indicates that the metal is on the surface while the loss of silicon from the larger clusters indicates that the metal is completely enclosed by silicon.

Our group has studied gas phase metal-PAH (polycyclic aromatic hydrocarbons) complexes in molecular beams by mass spectrometry and found that interesting sandwich complexes were made.²¹⁻²⁹

Over the years, the LVFR materials synthesis research project has evolved by improving instrument design and new analytical capabilities that have become available. Within the last five years, the most significant improvement was upgrading the vaporization laser. The original Compex laser had a maximum repetition rate of 100 Hz where the new LPX Pro laser can operate up to 400 Hz. This improvement allowed for increased material production. Availability of new mass spectrometers and Raman microscopes have improved the characterization of our materials. Other systems that have been studied or revisited but have not been completely explored or characterized will be discussed here. These systems include metal silicon clusters, theoretical calculations of titanium oxide with ethylenediamine and tetrahydrofuran (THF) ligands, titanium oxide acetonitrile synthesis, and the production of aluminum clusters.

Metal Silicon

The synthesis of metal silicon clusters in the LVFR have been attempted on different occasions throughout the years. Previous experiments in our group by Collin Dibble and Scott Akin utilized silane (1% SiH₄ in He) reactant gas, ablation of a Cr, Nb, or Ti rod, and acetonitrile as the ligand. The LD-TOF mass spectrum, shown in Figure 6.1 had peaks at m/z=299, 523, and 551 common to all three metals. These peaks are attributed to contamination in the silane gas, a silicon oxide cluster or some other source of contamination. There is a difference of 28 amu between the 551 and 523 peaks, which suggests there is one less silicon atom in the cluster corresponding to the 523 peak than that of the 551 peak. With the exception of the peak at m/z = 414 in the niobium spectrum, assignment of the remaining peaks in the spectra do not correspond to the masses of metal silicon clusters that are expected based on previous gas phase experiments. Masses of these expected clusters are found in Table 6.1. In the niobium spectrum, the peak at m/z = 414 and successive peaks at m/z = 442 and 470 can be assigned to (1,10,1), (1,11,1) and (1,12,1) respectively. These were the only peaks that can be assigned to the expected metal silicon clusters. However, no further analysis was done at the time to investigate these clusters.

My work on metal silicon clusters focused on theoretical calculations on the structures proposed in the literature and on synthesis method development. DFT and TD-DFT calculations focused on the structure of the singlet state encapsulated MSi₁₆ (M=Ti,

V, Cr) cluster and was calculated in Gaussian09 at the B3LYP/6-311+G(d,p) level³⁰ for comparison to the work of Li and coworkers.³¹ Compared to their work, the structures I calculated were qualitatively the same. However, the calculated binding energies, using the method described in the paper, were 20 eV higher (Table 6.2). Ligand addition to these clusters was also explored with ammonia (the smallest nitrogen containing ligand) and acetonitrile. The predicted spectra from these DFT and TD-DFT calculations (shown in Figures 6.1 through 6.25) can be compared to future experimental spectra collected for these clusters.

Due to safety concerns, alternatives to silane gas were considered for the synthesis of these systems. A few approaches were explored. The first was coating a silicon rod with chromium by vapor deposition. While the coating process was successful, the high intensity of ablation removes the layer of metal in a matter of minutes. This was not a viable method for the extended synthesis time necessary for sufficient material production. Next, vanadium wire was wrapped around a silicon rod for simultaneous ablation. While this was an improvement upon the vapor-coated rod, this was still not a sufficient method for synthesis. Vanadium wire is not the most cost-effective source for the amount of vanadium that is needed. The flexibility of the wire is also an issue. It is difficult to wrap around the Si rod and will break fairly easily. The final approach used custom targets purchased from Plasmaterials with 25% metal 75% silicon. The rod holder and source region were modified to accommodate a 1-inch diameter disk.

This method proved to be more successful. The UV/Visible spectrum for this sample, shown in Figure 6.26, had a weak absorption at 273 nm and a shoulder at

116

216 nm. In the ESI-TOF mass spectrum, shown in Figure 6.27, there was a high abundance of peaks in the 200-250 m/z range and a lower abundance of peaks in the 500-650 m/z range. The low mass region of the spectrum, as shown in Figure 6.28, did not produce mass assignments that corresponded to the expected clusters (as indicated by the red lines in the figure). There appeared to be a difference of 28 amu between alternating peaks suggesting clusters with varying amount of silicon atoms. The only logical metal silicon assignments were the bare clusters of (2,4), (2,5) and (2,6) for peaks at m/z= 214, 242, and 270 respectfully. However, divanadium clusters were not common in the previous gas phase experiments. Like the low mass range, expansion of the high mass range (Figure 6.29) also failed to show the expected clusters but exhibited a mass difference of 28 amu between peaks. Possible $V_x Si_y (MeCN)_z$ mass assignments in this range are shown in Table 6.3.

In addition to the V_xSi_y(MeCN)_z assignments, clusters of V_xO_y(MeCN)_z, Si_xO_y(MeCN)_z, VSi_xO_y(MeCN)_z, and V₂Si_xO_y(MeCN)_z were considered as alternative clusters that may be produced during synthesis. Peaks occurring at m/z= 200, 228, 256, and 284 can be assigned to either VSi_xO_y(MeCN) peaks or protonated V₂Si_x(MeCN) clusters with increasing amounts of silicon atoms, as labeled in Figure 6.28. The VSi target has a 99.9% purity with trace amounts of Ag, Bi, Co, Mg, Pb, Tl, Al, Ca, Cu, Mo, Sb, As, Cd, Fe, Ni, and Sn, but clusters with these metals were not considered. Polysiloxanes are common contaminants in ESI spectra and were also considered for possible peak assignements.³² The masses of these can be found in Table 6.4. The low mass region does not appear to contain any of these polysiloxane contaminants. The high mass region has peaks that overlap with potential polysiloxane peaks, but the full sequence of polysiloxane masses are not present in the experimental spectrum. While mass assignment is difficult, especially with vanadium being a single isotope transition metal, there does appear to be a mass separation of 28 amu in the spectra suggesting clusters with varying numbers of silicon atoms. Without further analysis, it is difficult to make mass assignments confidently.

Preliminary data for synthesis via a pre-made sputtering target appears promising for producing metal silicon clusters. More experiments are needed to explore optimum synthesis conditions and reproducibility as well as more extensive characterization with spectroscopy, mass spectrometry and electron microscopy. Sputtering targets of TiSi and CrSi were already purchased and are available for synthesis.

Titanium/Titanium Oxide

Titanium with ethylenediamine or THF as ligands was the first material synthesized in the LVFR apparatus.³³ Synthesis with ethylenediamine as a ligand produced a blue oil that was not soluble in several organic solvents, limiting the ability to characterize the material by methods other than mass spectrometry. The LD-TOF MS was the only mass spectrometer available at the time. In the spectrum, peaks corresponding to Ti(en)₃, Ti₂(en)₅ and Ti₃(en)₇ were observed. With THF used as the ligand, there was a high abundance of peaks corresponding to Ti₂O₂(THF)₄, Ti₂O₃(THF)₄, and Ti₂O(THF)₆. At the time, structures were predicted based on the stoichiometries and chemical intuition, but no theory was available to calculate the structures of these clusters. Due to the characterization limitations and lack of theory, it is of interest to revisit this system.

My work on this system focused on calculations of the cluster structures, done in Gaussian09 at the B3LYP/def2svp level³⁰ and are shown in Figures 6.30 through 6.46 with relative energies shown in Table 6.5. The optimized structures are similar to the originally suggested structures with the exception of the $Ti_3(en)_7$ cluster. Calculations on this cluster did not result in a chemically logical structure. More investigation is needed into alternate isomers or different functionals/basis sets to accurately determine the structure of the $Ti_3(en)_7$ cluster.

The synthesis of titanium oxide with acetonitrile as ligands was explored by vaporizing a titanium rod with a flow of 5% oxygen seeded helium. The UV/Visible spectrum, shown in Figure 6.47, appears to be very similar to the VSi absorption spectrum. Investigation into this is needed. It may be that we picked up a contaminate in the system or from the acetonitrile. This only occurred in the UV/Visible and not in the mass spectra of these two systems. The LD-TOF mass spectrum, shown in Figure 6.48, had a low abundance of peaks in the 400-550 m/z region. Mass assignments of these peaks are shown in Table 6.7, with cluster sizes following the bulk TiO₂ stoichiometry shown in bold. Titanium with acetonitrile in a flow of pure helium was investigated, but there were no significant features observed in the UV/Visible absorption spectrum as shown in Figure 6.49. This system needs more synthesis experiments to determine if nanoclusters can be produced.

The original $Ti_x(en)_y$ and $Ti_x(THF)_y$ clusters were air sensitive, so a new freezepump-thaw solvent chamber was developed and fabricated for use during titanium ethylenediamine or THF synthesis to eliminate atmospheric oxygen from entering the system from ligand addition. By synthesizing the clusters again with the new laser system, more material may be available for analysis by other spectroscopy techniques or ESI-TOF MS. However, synthesis with ethylenediamine, THF, or acetonitrile has not been further explored.

Aluminum

Aluminum acetonitrile clusters were previously synthesized and though they can be reproducibly made, it is quite a difficult process.³⁴ These clusters have only been made with the highest laser powers available from the vaporization laser and ablation should occur for about 30 minutes before collecting material to burn off any oxides that have formed on the surface of the rod. The original mass spectrum of high synthesis laser power showed peaks in the high mass range (above 400 m/z) that could have multiple mass assignments, but due to the resolution of the instrument, could not be assigned definitively. With the addition of the Comstock, Inc. LD-TOF mass spectrometer, the capability of higher resolution mass spectrometry became available. I was able to synthesize small aluminum clusters as shown in the higher resolution mass spectrum in Figure 6.50. No peaks in the 400 m/z range or higher were observed. However, I believe the larger clusters should be able to be reproduced again with higher laser power. After maintenance on the apparatus during molybdenum oxide experiments where the laser beamsplitter and UV grade silica window into the apparatus were replaced, a significant increase in power was achieved. With this increase in power, new aluminum synthesis runs should result in the larger clusters.

Conclusions

The laser vaporization flow tube reactor apparatus is an innovative method for synthesizing nanomaterials. Method development and potimization which is in a continual state of gradual development. The systems studied here have shown promise but still have a significant amount of work left to completely understand the synthesis conditions and fully characterize the material. However, there are systems or conditions for systems that have not been successful, these include the reproducibility of CoO(MeCN) and initial synthesis of MnO. Other systems explored by our group, but not discussed here include: Cr(Coronene), WO(MeCN), VC(MeCN), and VOC(MeCN). Many systems have been surveyed but many more remain to be explored.

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Figure 6.1. LD-TOF mass spectra of $Cr_xSi_y(MeCN)_z$, $Nb_xSi_y(MeCN)_z$, and $Ti_xSi_y(MeCN)_z$ generated by Collin Dibble and Scott Akin. Red dashed lines indicate peaks common to all three spectra but are attributed to a contamination in the silane gas.

Cluster	Si ₇	Si_{10}	Si_{12}	Si 15	Si_{16}
Si (28 amu)					
Sin	196	280	336	420	448
Si _n (MeCN)	237	321	377	461	489
Si _n (MeCN) ₂	278	362	418	502	530
Si _n (MeCN) ₃	319	403	459	543	571
Ti (48 amu)					
TiSin	244	328	384	468	496
TiSi _n (MeCN)	285	369	425	509	537
TiSin(MeCN)2	326	410	466	550	578
TiSin(MeCN) ₃	367	451	507	591	619
V (51 amu)					
VSin	247	331	387	471	499
VSi _n (MeCN)	288	372	428	512	540
VSin(MeCN)2	329	413	469	553	581
VSi _n (MeCN) ₃	370	454	510	594	622
Cr (52 amu)					
CrSin	248	332	388	472	500
CrSi _n (MeCN)	289	373	429	513	541
CrSi _n (MeCN) ₂	330	414	470	554	582
CrSi _n (MeCN) ₃	371	455	511	595	623
Nb (93 amu)					
NbSin	289	373	429	513	541
NbSi _n (MeCN)	330	414	470	554	582
NbSi _n (MeCN) ₂	371	455	511	595	623
NbSi _n (MeCN) ₃	412	496	552	636	664

Table 6.1. Nominal masses of common metal silicon clusters with various numbers of acetonitrile ligands.



Figure 6.2. $TiSi_{16}$ cluster calculated at the B3LYP/6-311G+(d,p) level. Bond lengths in angstroms.



Figure 6.3. VSi_{16} cluster calculated at the B3LYP/6-311G+(d,p) level. Bond lengths in angstroms.



Figure 6.4. $CrSi_{16}$ cluster calculated at the B3LYP/6-311G+(d,p) level. Bond lengths in angstroms.

Table 6.2. Binding energies of MSi_{16} clusters calculated at the B3LYP/6-311G+(d,p) level with zero-point corrected energies. Compared to the binding energies calculated by Li and coworkers (reference 31).

Cluster	2n+1	Total Energy	Binding Energy	Reference 31
		(hartrees)	(eV)	(eV)
Ti	1	-849.290002		
V	1	-943.828778		
Cr	1	-1044.223886		
Si ₁₆	1	-4632.151690		
TiSi ₁₆	1	-5481.718566	-77.1	-55.737
VSi ₁₆	1	-5576.257545	-75.6	-56.641
CrSi ₁₆	1	-5676.707193	-75.6	-54.609



Figure 6.5. Predicted infrared spectra for MSi_{16} clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.6. Predicted Raman spectra for MSi_{16} clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.7. Predicted UV/Visible spectra for MSi_{16} clusters. Calculated at the B3LYP/6-311G+(d,p) level with 20 nm Lorentzian broadening.



Figure 6.8. $TiSi_{16}(NH_3)_x$ clusters calculated at the B3LYP/6-311G+(d,p) level.



Figure 6.9. Predicted infrared spectra for $TiSi_{16}(NH_3)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.10. Predicted Raman spectra for $TiSi_{16}(NH_3)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.


Figure 6.11. $VSi_{16}(NH_3)_x$ clusters calculated at the B3LYP/6-311G+(d,p) level.



Figure 6.12. Predicted infrared spectra for $VSi_{16}(NH_3)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.13. Predicted Raman spectra for $VSi_{16}(NH_3)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.14. $CrSi_{16}(NH_3)_x$ clusters calculated at the B3LYP/6-311G+(d,p) level.



Figure 6.15. Predicted infrared spectra for $CrSi_{16}(NH_3)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.16. Predicted Raman spectra for $CrSi_{16}(NH_3)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.17. $TiSi_{16}$ (MeCN)_x clusters calculated at the B3LYP/6-311G+(d,p) level.



Figure 6.18. Predicted infrared spectra for $TiSi_{16}(MeCN)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.19. Predicted Raman spectra for $TiSi_{16}(MeCN)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.20. $VSi_{16}(MeCN)_x$ clusters calculated at the B3LYP/6-311G+(d,p) level.



Figure 6.21. Predicted infrared spectra for $VSi_{16}(MeCN)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.22. Predicted Raman spectra for $VSi_{16}(MeCN)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.23. $CrSi_{16}(MeCN)_x$ clusters calculated at the B3LYP/6-311G+(d,p) level.



Figure 6.24. Predicted infrared spectra for $CrSi_{16}(MeCN)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.25. Predicted Raman spectra for $CrSi_{16}(MeCN)_x$ clusters. Calculated at the B3LYP/6-311G+(d,p) level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.26. UV/Visible absorption spectrum of $V_x Si_y (MeCN)_z$ synthesized from a VSi sputtering target.



Figure 6.27. Full range ESI-TOF mass spectrum of $V_x Si_y (MeCN)_z$ synthesized from a VSi sputtering target



Figure 6.28. Low mass range ESI-TOF mass spectrum of $V_x Si_y (MeCN)_z$ synthesized from a VSi sputtering target. Red lines indicate masses of expected clusters.



Figure 6.29. High mass range ESI-TOF mass spectrum of $V_x Si_y (MeCN)_z$ synthesized from a VSi sputtering target. Red lines indicate masses of expected clusters.

Peak	Cluster Size	Peak	Cluster Size
(m/z)	$V_x Si_y (MeCN)_z^+$	(m/z)	V _x Si _y (MeCN) _z
506	(1,6,7)	576	(2,14,2)
	(4,2,6)		(5,10,1)
520	(2,12,2)	582	(3,8,5)
	(5,8,1)		(6,4,4)
534	(1,7,7)	596	(1,18,1)
	(4,3,6)		(2,3,10)
			(4,14,0)
547	(1,6,8)		
	(4,2,7)	607	(1,14,4)
			(4,10,3)
554	(3,7,5)		
	(3,6,4)	624	(1,19,1)
			(2,4,10)
561	(2,12,3)		(4,15,0)
	(5,8,2)		
		638	(3,10,5)
568	(1,17,1)		(6,6,4)
	(2,2,10)		
	(4,13,0)		

Table. 6.3. Possible $V_x Si_y (MeCN)_z$ mass assignments for the high mass range ESI spectrum from VSi sputtering target. Masses not listed do not appear to contain $V_x Si_y (MeCN)_z$.

Cluster	Ion	Mass
$(C_2H_6SiO)_5$	$[M+H-CH_4]^+$	355.06994
	$[M+H]^+$	371.10124
	$[M+NH_4]^+$	388.12779
$(C_2H_6SiO)_6$	$[M+H-CH_4]^+$	429.08873
	$[M+H]^+$	445.12003
	$[M+NH_4]^+$	462.14658
(C ₂ H ₆ SiO) ₇	$[M+H-CH_4]^+$	503.10752
	$[M+H]^+$	519.13882
	$[M+NH_4]^+$	536.16537
(C ₂ H ₆ SiO) ₈	$[M+H-CH_4]^+$	577.12631
	$[M+H]^{+}$	593.17567
	$[M+NH_4]^+$	610.18416
(C ₂ H ₆ SiO) ₉	$[M+H-CH_4]^+$	651.14510
	$[M+H]^{+}$	667.17640
	$[M+NH_4]^+$	684.20295

Table 6.4. Masses of polysiloxanes, a common ESI contaminant. Reproduced from Reference 32.



Figure 6.30. Overview of calculated $Ti_x(en)_y$ clusters.



Figure 6.31. Lowest energy Ti(en)₃ structure in the triplet state calculated at the B3LYP/def2svp level. Bond lengths in angstroms.



Figure 6.32. Lowest energy $Ti_2(en)_5$ structure in the singlet state calculated at the B3LYP/def2svp level. Bond lengths in angstroms.



Figure 6.33. Lowest energy calculated $Ti_3(en)_7$ structure at the B3LYP/def2svp level. Dashed lines were added to indicate potential bonds that were not present in the final calculated structure. Bond lengths in angstroms.

Cluster	2n+1	Total Energy (hartrees)	Relative Energy (kcal/mol)	
Ti(en) ₃	1	-1420.130937	+29.1	
Ti(en) ₃	3	-1420.177349	0.0	
Ti ₂ (en) ₅	1	-2650.119751	0.0	
Ti ₂ (en) ₅	3	-2650.044080	+47.5	
Ti ₃ (en) ₇	1	-3879.883427	+27.2	
Ti ₃ (en) ₇	3	-3879.926737	0.0	

Table 6.5. Titanium ethylenediamine relative energies calculated at the B3LYP/def2svp level with zero-point corrected energies.



Figure 6.34. Predicted infrared spectra for the lowest energy $Ti_x(en)_y$ clusters. Calculated at the B3LYP/def2svp level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.35. Predicted Raman spectra for the lowest energy $Ti_x(en)_y$ clusters. Calculated at the B3LYP/def2svp level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.36. Predicted UV/Visible spectra for the lowest energy $Ti_x(en)_y$ clusters. Calculated at the B3LYP/def2svp level with 20 nm broadening.



Figure 6.37. Overview of $Ti_2(THF)_4$ clusters. Above are the optimized structures, calculated at the B3LYP/def2svp level, of three different starting isomers. Relative energies are given in kcal/mol.



Figure 6.38. Overview of $Ti_2(THF)_6$ clusters. Above are the optimized structures of three different starting isomers, calculated at the B3LYP/def2svp level. Relative energies are given in kcal/mol.



Figure 6.39. Lowest energy calculated $Ti_2(THF)_4$ structure at the B3LYP/def2svp level. Bond lengths in angstroms.



Figure 6.40. Lowest energy calculated $Ti_2(THF)_6$ structure at the B3LYP/def2svp level. Bond lengths in angstroms.

Cluster	2n+1	Total Energy	Relative Energy	
		(hartrees)	(kcal/mol)	
Ti ₂ THF ₄	1	-2853.113831	+35.7	
Ti ₂ THF ₄	3	-2853.170725	0.0	
Ti ₂ THF ₄ cross	1	-2853.116814	+33.8	
Ti ₂ THF ₄ cross	3	-2853.168063	+1.7	
Ti ₂ THF ₄ planer	1	-2853.166687	+2.5	
Ti ₂ THF ₄ planer	3	-2853.158099	+7.9	
Ti ₂ THF ₆	1	-3166.881874	+27.0	
Ti ₂ THF ₆	3	-3166.923376	+0.9	
Ti ₂ THF ₆ cross	1	-3166.862697	+39.0	
Ti ₂ THF ₆ cross	3	-3166.924788	0.0	
Ti ₂ THF ₆ tetra	1	-3166.902050	+14.3	
Ti ₂ THF ₆ tetra	3	-3166.922772	+1.3	

Table 6.6. Titanium tetrahydrofuran relative energies calculated at the B3LYP/def2svp level with zero-point corrected energies.



Figure 6.41. Predicted infrared spectra for the lowest energy $Ti_2(THF)_4$ isomers. Calculated at the B3LYP/def2svp level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.42. Predicted Raman spectra for the lowest energy $Ti_2(THF)_4$ isomers. Calculated at the B3LYP/def2svp level with 50 cm⁻¹ Lorentzian broadening.


Figure 6.43. Predicted UV/Vis spectra for the lowest energy $Ti_2(THF)_4$ isomers. Calculated at the B3LYP/def2svp level with 20 nm Lorentzian broadening.



Figure 6.44. Predicted infrared spectra for the lowest energy $Ti_2(THF)_6$ isomers. Calculated at the B3LYP/def2svp level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.45. Predicted Raman spectra for the lowest energy $Ti_2(THF)_6$ isomers. Calculated at the B3LYP/def2svp level with 50 cm⁻¹ Lorentzian broadening.



Figure 6.46. Predicted UV/Vis spectra for the lowest energy $Ti_2(THF)_6$ isomers. Calculated at the B3LYP/def2svp level with 20 nm Lorentzian broadening.



Figure 6.47. UV/Visible spectrum of Ti_xO_y(MeCN)_z.



Figure 6.48. LD-TOF mass spectrum of $Ti_xO_y(MeCN)_z$.

Peak (m/z)	Cluster Size $Ti_xO_y(MeCN)_z^+$
415	(1,5,7) (2,2,7)
431	(3,0,7) (1,6,7) (2,3,7)
443	(1,17,3) (2,14,3) (3,11,3) (4,8,3) (5,5,3) (6,2,3)
459	(7,0,3) (1,18,3) (2,15,3) (3,12,3) (4,9,3) (5,6,3) (6,3,3)
488	(1,7,8) (2,4,8) (3,1,8)

Table 6.7. Possible mass assignments for $Ti_xO_y(MeCN)_z$. Peaks not listed here do not appear to contain $Ti_xO_y(MeCN)_z$.



Figure 6.49. UV/Visible spectrum of Ti_x(MeCN)_y.



Figure 6.50. High resolution LD-TOF mass spectrum of Al(MeCN) clusters.

CHAPTER 7

CONCLUSIONS

The experiments discussed here have shown that the laser vaporization flowtube reactor (LVFR) is a viable method for producing new materials with stoichiometries unlike those produced by more traditional methods. They have also shown that the LVFR can produce both nanoclusters and nanoparticles. The ligand-coated clusters captured in solution were characterized by various forms of mass spectrometry, spectroscopy, electron microscopy, and computational chemistry. Ligand-coated chromium oxide and molybdenum oxide nanomaterials have been shown to be stable under ambient conditions for months at a time. The material can be dried down into a powder and, because of the ligand coating, can be redissolved in acetonitrile and other polar solvents such as water, methanol, or acetone.

Characterization of LVFR synthesized chromium oxide material indicated a complex mixture of cluster sizes were produced. While no one cluster size can be matched to the experimental spectroscopic data collected, our material was consistent with spectroscopic data from other chromium oxide nanomaterials, particularly in the UV/Visible absorption and Raman spectra. Theoretical calculations suggested that the larger clusters with more open ring-like structures have predicted spectra that most closely resemble the experimental data.

LVFR synthesis of molybdenum oxide nanomaterial have produced nanorods that are much smaller than traditional synthesis methods. Characterization of these nanorods have shown that they have optical and electronic properties similar to those of other molybdenum oxide nanomaterials. The band gap of the nanorods was determined to be 3.48 eV. The nanorods have shown increased catalytic activity compared to commercial material.

While these experiments and previous experiments with titanium and vanadium have shown the ability produce to transition metal oxide materials, the LVFR synthesis method can be applied to other systems. Other nanomaterials that have been studied are silver nanoparticles, aluminum nanoclusters, vanadium oxycarbide nanowires, metal-PAH complexes, metal-carbide, and metal-silicon complexes. The efficiency of the synthesis varies from system to system. The ability to scale up material production has greatly increased since the original work on titanium. However, an increase in production is still needed for some characterization techniques such as powder x-ray diffraction (XRD) or diffuse reflectance, which require much more material than the few milligrams we can produce.

While a lot of work has been put into synthesizing these materials and finding systems that can be produced with the LVFR, there is still much we don't understand and what specific experimental parameter leads to one cluster size or another, or nanocluster versus nanoparticle synthesis. More research is needed to further understand optimized synthesis conditions, appropriate ligands, and more comprehensive characterization and isolation of cluster sizes for these materials.

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More investigation into these experimental parameters, such as laser power, ligands, pressures, etc. are needed. We have found the laser power to be a very important parameter in producing nanoclusters and nanoparticles of a particular size. As shown in the synthesis of chromium oxide and molybdenum oxide materials, laser powers below 100 mJ/pulse do not usually produce material and increasing laser power can preferentially make one cluster size in a higher abundance than others. Experiments that are run without ligand or that introduce ligand at the point of vaporization do not usually produce soluble material. Many conditions were explored during the synthesis of chromium oxide and molybdenum oxide, but there are more experimental parameters that could be considered. Intense focus on the experimental conditions can help sort out the exact parameters needed to grow materials of a specific size and to understand how changing a parameter affects the size of nanomaterial produced.

More work on the separation and isolation of cluster sizes is needed for complex solutions like chromium oxide. Although preliminary HPLC experiments have confirmed multiple components in the chromium oxide solution, more work is needed. Larger amounts of material are necessary for separation to be left with enough isolated material to spectroscopically analyze. An alternative to physical separation is to identify the various cluster isomers by ion mobility mass spectrometry. Ion mobility experiments would allow for the separation of compact cages from long chains or large open rings. Investigating these areas can help us better understand these unique and fascinating materials.

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