RICE UNIVERSITY

Size and Shape Control of Colloidal Aluminum Nanocrystals for UV Plasmonics Applications

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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April 2017
ABSTRACT

Synthesis of Aluminum Nanocrystals

by

Michael J. McClain

Metallic nanocrystals show tremendous promise in photocatalysis, distillation, and chemical sensing applications. This is due to their unique optical properties that arise from the collective oscillation of the conduction electrons, known as the plasmon resonance. However, most nanocrystal research is on noble metals such as gold or silver which have issues for larger scale applications because of their cost and intrinsic properties. For example, gold works well for visible and near-IR applications but cannot support an ultraviolet plasmon resonance due to interband transitions. The UV region is of great interest for many applications including ultrasensitive detection of organic molecules, photocatalysis, sterilization and remediation. While silver can support a UV plasmon resonance it is prone to complete oxidation. In this thesis, I demonstrate size and shape control of colloidal aluminum nanocrystal.

Aluminum is the most abundant metal in the earth’s crust and can support a UV plasmon resonance. Additionally, aluminum forms a 3-5nm self-limiting oxide layer that keeps the nanocrystal stable for several months under ambient conditions. I demonstrate that by choosing appropriate solvent ratios, aluminum nanocrystal size
can be tuned from 50 nm to 220nm, tuning the plasmon resonance from 250 to 700 nm. Then, I use FT-IR spectroscopy to show the aluminum hydride-adduct exchanges ligands with coordinating solvents in solution. We found that bidentate coordinating solvents lead to polymeric aluminum hydride structures which in turn lead to smaller nanocrystals. We also observed increased twinning in reactions with multi-coordinating tertiary amine solvents. This work provides the basis for rational design of air-sensitive metal nanocrystals and allows for a facile route to control the size of aluminum nanostructures.
Acknowledgments

First off, I’d like to thank Professor Naomi J. Halas for her mentorship, leadership, and patience. She taught me that every failed experiment is not a failure but a lesson. Despite a few hundred of these lessons, she continued to believe in my work and her tireless work ethic inspired me to achieve my goals.

I’d also like to thank Professor Whitmire who gave me a lab space. He always challenged me to be precise with experiments and avoid jumping to conclusions in the complex field of nanochemistry.

Next, I’d like to thank Professor Nordlander for his collaborative work and excellent instruction in the Electrodynamics and Nanophotonics course. Thank you for making the fundamentals of calculating and modeling plasmonic approachable for a synthetic chemist. I’d also like to thank his former students: Dr. Alejandro Manajavacas, Dr. Lifei Liu, and Dr. Yao Cui for their work.

I’d like to thank Dr. Christopher DeSantis for his work as a mentor and colleague.

I’d also like to thank all the past and present Halas lab group members that I’ve worked with: Dr. Nathan Hogan, Dr. Andie Schlather, Dr. Britt Lassiter, Dr. Mark Knight, Dr. Ryan Huschka, Dr. Shaunak Muhkerjee, Dr. Oara Neumann, Dr. Nicholas King, Dr. Fangfang Wen, Dr. Jared Day, Dr. Yu Zhang, Dr. Lisa Brown, Dr. Surbhi Lal, Dr. Amanda Goodman, Dr. Ali Sobhani, Ben Cerjen, David Renard, Benjamin Clark, Samuel Gottheim, Liang Liang Dong, Chao Zhao, Dayne Swearer, Linan Zhou, and Adam Lauchner.

Lastly, I’d like to thank my family for their support: Mom, Dad, Jim, and Will.
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## Nomenclature

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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>LAH</td>
<td>Lithium aluminum hydride</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>TMA</td>
<td>Trimethylamine</td>
</tr>
<tr>
<td>DMEAA</td>
<td>N,N-dimethylethylamine alane</td>
</tr>
<tr>
<td>MPDA</td>
<td>1-methylpyrrolidine alane</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TEDA</td>
<td>Tetraethylenediamine</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>CL</td>
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<tr>
<td>EELS</td>
<td>Electron-energy loss spectroscopy</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscope</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized surface plasmon resonance</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>MMOPRH</td>
<td>N-methylmorpholine</td>
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<td>TMEDA</td>
<td>N,N,N’,N’-tetramethylethylenediamine</td>
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<td>TEA</td>
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Chapter 1

Background

1.1. Metal Nanocrystal Synthesis

Noble metal nanoparticles are used extensively for applications such as photocatalysis or biological and chemical sensing.\(^1\)-\(^8\) Interest in these nanoparticles has been based largely on their vivid optical properties, which are due to their collective electronic resonances, known as localized surface plasmons. The surface plasmon resonance depends on the size, shape, and material of the nanocrystal so the morphology of a nanocrystal is crucial to its performance in applications involving light. Efforts to control the size and shapes of nanoparticle have resulted in a plethora of nanoparticle shapes: from platonic solids such as octahedron and icosahedron, to anisotropic structures like nanorods, and to more complex and exotic structures such as branched nanoparticles.\(^9\)-\(^14\) The goal of a nanochemist is to be able to rationally predict the structure of a nanoparticle from a set of experimental parameters. This goal can be daunting as many shapes can result from thermodynamic and kinetic
control (Figure 1). The purpose of this section is to outline several key theories and strategies in nanosynthesis.

**Figure 1 - Shapes separated based on if they occur thermodynamic and kinetic control from Ref. 19.**

Metal nanocrystal reactions appear simple. Research articles will typically show an elementary reaction between metal salt and a reducing agent; however, this idealized picture can be more complicated. For example, a precursor is not always a monomer unit in solution and the existence of polymer species may affect the resulting nanocrystals. So it helps to have a mechanism to understand the steps of nanocrystal growth. A well-regarded mechanism is the LaMer mechanism that was developed from thorough investigation of the synthesis of monodisperse sulfur colloids. In the LaMer mechanism, a precursor is reduced or decomposed to form
atoms. These atoms increase in concentration over time until they reach a point of supersaturation. Then, the atoms rapidly aggregate into small clusters called nuclei. As more atoms are supplied from decomposing precursor, the nuclei evolve into seeds and then continue to grow into nanocrystals. The shape of the seeds is an indicator of the morphology of resulting nanocrystals.  

Scientists have employed numerous experimental strategies for altering the growth of metallic nanocrystals by modifying seeds. As seeds dictate the resulting morphology and size distribution of nanocrystals, homogeneity in seeds is paramount. Homogeneity in seeds is achieved by having a single nucleation event, or “burst nucleation”. If burst nucleation is difficult to achieve, cycles of oxidative dissolution and reductive growth can drastically improve monodispersity. Another aspect of nanoparticle growth is inducing anisotropy. There is evidence that surfactants can stabilize certain facets of seeds which results in anisotropic growth. Other methods include lattice mismatch growth, for example, using Au seeds to grow Cu nanorods. Also, a small impurity of another metal can also induce anisotropy such as Ag in Au seeds. While the precursors and materials change, the fundamentals of crystal growth are applicable to all nanocrystal reactions.

### 1.2. Aluminum Nanoparticle Synthesis

The reaction between a metal salt and a reducing agent to synthesis nanocrystals works for the noble metals (Ag, Cu, Au, Pd, Pt) as well as some poor metals (In, Ga, Mn) because they have high enough reduction potentials that traditional reducing agents such as NaBH₄, LiAlH₄, or alkyl-alkaline earth metals can
reduce them. Also, an advantage of these reducing agents is they may be dissolved in solution for a homogeneous reaction which is crucial for achieving monodisperse shapes and sizes. Unfortunately, the reducing agents listed above do not work for aluminum because aluminum has a much lower reduction potential (-1.66 V). Furthermore, aluminum salt, AlX₃ (X = Cl, Br, I, other anions), reacts with LAH to form AlH₃ and alkyl-alkaline earth metals (such as n-BuLi) to form alkyl-aluminum (AlR₃). Both AlH₃ and AlR₃ are stable under an inert atmosphere. There is some work on aluminum salts reduced by sodium metal and we tried sodium napthalenide reduction, however were only obtained heavily aggregated and with poorly define facets. In the end, it comes down to decomposing an aluminum hydride or alkyl aluminum. In this chapter, I will cover current colloidal aluminum nanoparticle synthesis papers.

The first report of synthesis of aluminum nanoparticles was in 1998 by Haber and Buhro. They reported two methods for preparation. Method A is decomposition of alane with 165°C and Method B is decomposition with a titanium catalyst. Method A proved to be inconvenient as it was difficult to remove large amounts of LiCl from the reaction without the exothermic oxidation of the nano-Al. The size of the nanocrystals were determined using Scherrer analysis of the XRD linewidths. From the mean choerence length of sixteen trials, they guessed the nanocrystals were 160 ± 50 nm. TEM analysis of the nanocrystals revealed two major products: heavily aggregated non-faceted morphologies and polyhedral crystallites (tetrahedra, octahedra, and cuboctahedra). The second method could proceed with or without a
catalyst and then requiring heat and produced nanocrystals with similar morphologies.

Subsequent papers on aluminum nanocrystals focused on capping the surface with alkyl chains to maximize the amount of active aluminum content for use of the powder as rocket propellant. The results of these papers in context with size and morphological control of Al nanoparticles is summarized here. In 2005, Jouet et al. added perfluorocarboxylic acids to TMA-alane in diethyl ether to produce 20-150 nm nanoparticles. In 2009, Fernando et al. synthesized 20-70 nm Al nanoparticles by sonicingating a solution of DMEAA in dodecane with oleic acid and ~30 nm Al nanoparticles in toluene with epoxide as a capping agent. Then in 2011, Meziani et al. decomposed DMEAA and N-methylpyrrolidine (MPD) in toluene with perfluorotetradecanoic acid as a capping agent. They noted that DMEAA decomposed more readily than MPDA and resulted in more homogeneous nanoparticles and also higher yield. They attributed the yield disparity to the difference in stability, DMEAA was less stable so more of the precursor decomposed over a given time to produce Al NPs. They also noted that if they delayed the addition of the capping agent, the yield increased further. They concluded with morphological control of aluminum nanoparticles requires control of the alane decomposition.

A paper in 2014 demonstrated that monodisperse aluminum nanoparticles can be synthesized in trimethylbenzene with triphenylphosphine as a capping agent. This is the first aluminum nanoparticle synthesis paper that does not use a reactive capping agent, one that reacts with alane to form a stable alane complex, to form nanoparticles. One issue is they claim the aluminum nanoparticle is surrounded
by an amorphous PPh$_3$ layer, rather than a Al$_2$O$_3$ on grounds the surrounding layer is not crystalline. There is no other evidence to back up this claim. However, their lack of a reactive capping agent is very relevant to our work.

Overall, the only discernable trend between all the mentioned papers is Al nanoparticles need some sort of capping or coordinating species for homogeneous nanoparticle growth. After my work on size control of aluminum nanocrystals with THF and dioxane in the absence of a capping agent (Chapter 2), I began researching the chemistry of alanes. In the next section, I highlight several of the papers that became the foundation for my research in Chapter 3.

1.3. Alane Chemistry

The chemistry of aluminum hydride, specifically Lewis base-alane complexes, received a lot of attention for its role in CVD and hydrogen storage technology.$^{28,29}$ In this chapter, I will highlight several of the major papers that are relevant to aluminum nanocrystal. Specifically, papers that investigate the stability of alane as a function of its ligands.

There were several important observations on the chemistry of aluminum hydride that began in the 50s and 60s. The crystal structure of alane was resolved in 1969 and while alane does not have an fcc structure, the geometry of the Al atoms is the same as in the metal except the Al-Al distance is larger: 4.45 Å in alane and 2.81 Å in aluminum metal.$^{30}$ In 1962, Ehrlich characterized lewis base-alane complexes in ethereal and tertiary amine solvents with infrared spectroscopy.$^{31}$ Specifically, he looked at alane coordinated with different alane:base ratios of trimethylamine (TMA),
diethylether, and tetrahydrofuran (THF) and the shifts of the Al-H stretch in these solvents. His key observation was TMA:alane would readily coordinate with THF but not diethylether due to steric.

Gavrilenko applied this knowledge to the decomposition of Lewis base-alane complexes $\text{AlH}_3$-D (D = diethyl ether, THF, and trimethylamine). He noted that the decomposition rate decreased with increasing donor strength of the ligand. One important observation that $\text{AlH}_3$-THF in a solution of THF decomposed slower than $\text{AlH}_3$-N(CH$_3$)$_3$ in diethylether. Additionally, he noted that Zr, V, and Ni catalysts were one to two orders of magnitude less effective at decomposing alanes. The exact role of the titanium catalyst is unknown, but a review by Frankcombe highlights several theories backed with experimental evidence. After this paper, there is little documented interest in understanding the role of the ligand in alanes thermal decomposition reaction.

Alane chemistry saw a resurgence in the 2000s as it showed promise as a hydrogen storage material. Graetz et al. demonstrated that alanes could be regenerated from Al doped with Ti, H$_2$, and TEDA. After this result, several groups began looking into alane-ligand complex stability to optimize this cyclic process. In 2011, Wong et al. calculated the Gibbs free energy of many alane-ligand complexes. They found that alanes can form several geometries: 4-coordinate about the Al monomer, a 5-coordinate bis complex, and a bridging hydride dimer. The geometry of the alane depends on the strength of the ligand and its sterics. They went on to calculate the Al-H IR stretching frequency for several amines and showed the
frequencies were well separated for the different possible geometries of alanes. Thus, proving IR as a useful tool for probing the alane-ligand environment.

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Table 1 - pKₐ values of decomposition temperatures and melting points for AlH₃ complexes adapted from ref. 29.

Humpheries et al. synthesized and characterized a library of alane-ligand complexes to determine a relationship between ligand and alane structure (Table 1).³⁷,³⁸ They noted an important trend that became the foundation for the work presented in Chapter 4: alanes that coordinate with multi-coordinating ligands that result in polymeric structures are more stable. As mentioned in a previous section, altering the stability of a metal precursor may affect the growth of nanocrystals.
The work from these groups are vital for understanding the complexity of aluminum nanocrystal research. Although it is difficult to predict the relationship between precursor and resulting nanocrystal, having a firm understanding of your materials can help you notice trends in morphology.
Chapter 2

Aluminum Nanocrystals

We demonstrate the facile synthesis of high purity aluminum nanocrystals over a range of controlled sizes from 70 nm to 220 nm diameter, with size control achieved through a simple modification of solvent ratios in the reaction solution. The monodisperse, icosahedral and trigonal bipyramidal nanocrystals are air-stable for weeks, due to the formation of a 2-4 nm thick passivating oxide layer on their surfaces. We show that the nanocrystals support size-dependent ultraviolet and visible plasmon modes, providing a far more sustainable alternative to gold and silver nanoparticles currently in widespread use.

2.1. Introduction

Noble metal nanoparticles are used extensively for applications such as photocatalysis or biological and chemical sensing.\textsuperscript{1-8} Interest in these nanoparticles
has been based largely on their vivid optical properties, which are due to their collective electronic resonances, known as localized surface plasmons. Exquisite size and shape control has been achieved in the synthesis of noble metal nanoparticles such as gold, silver, and platinum, but the intrinsic properties and high cost of these noble metals present significant limitations for large-scale use.\textsuperscript{7,14,39} Gold nanoparticles have been of interest in applications involving visible and near-infrared light, and while the plasmon resonance of silver can also be excited at wavelengths that extend into the ultraviolet region of the spectrum, its conversion from silver to silver oxide limits its long-term stability. The UV region ($\lambda = 100$ nm – 400 nm) is of great interest in numerous applications; for example, most organic molecules have a strong absorption in the ultraviolet, allowing for ultrasensitive chemical sensing. Short wave UV light ($\lambda < 280$ nm) is capable of breaking organic bonds, which is key to sterilization, remediation, and photocatalysis applications.

Aluminum is the most abundant metal in the earth’s crust and can support a UV plasmon resonance.\textsuperscript{3–5,7} Recent research on lithographically-fabricated aluminum nanostructures demonstrated that the plasmon resonance is highly sensitive to oxygen content, redshifting and attenuating the plasmon resonance with increasing oxygen content.\textsuperscript{4,40} Chemical methods for the synthesis of Al nanoparticles have involved the thermal decomposition of an aluminum hydride with a titanium catalyst, but size and shape control have proven to be problematic with this approach.\textsuperscript{24–26,32,41–45} In this letter we report the facile synthesis of highly regular, faceted aluminum nanocrystals with controllable nanocrystal diameters ranging from 70 to
greater than 200 nm. The optical properties of individual Al nanocrystals were measured using dark field spectroscopy, cathodoluminescence (CL), and electron-energy loss spectroscopy (EELS), which clearly show the size-dependent, continuous tuning of the optical resonance from ultraviolet to the visible region of the spectrum with increasing nanocrystal diameter. The Al nanocrystals are terminated with a self-limiting, 2-4 nm oxide layer, which imparts stability: an important property that can ultimately enable their use in many different types of applications.

2.2. Materials and Methods

The aluminum nanocrystals were synthesized by adding a capping agent to the reaction shown in Figure 4a. The nanocrystals shown were synthesized using Schlenk line and glove box techniques. All solvents and reagents were purchased from Sigma Aldrich and dried and distilled under inert atmosphere before use. 1,4-dioxane and Tetrahydrofuran (THF) were added to a dry Schlenk flask under Ar atmosphere. Varying volume fractions of THF and 1,4-dioxane were added to equal 25 mL of solvent. The flask was heated in a 40°C oil bath. The reaction takes more than 12 hours to complete at room temperature, and less than half an hour at 70°C. However, particles made at 40°C, although it took 2 hours for the reaction to complete, showed better size distributions than those obtained at the higher reaction temperature 70°C. While the solvent was stirring, 6.5 mL of 0.5 M N,N-dimethylethylamine alane was added. 0.5 mL of a 3.3mM solution of titanium (IV) isopropoxide in toluene was added rapidly via syringe. The role of titanium is not explicitly clear, however, a variety of plausible mechanisms in similar types of reactions have been proposed.32,46 After 2.5
minutes, 0.5 mL of a 250 mM solution of oleic acid in 1,4-dioxane was added rapidly via syringe and the solution turns from clear to brown. The reaction proceeded for 2 hours during which the reaction turned from black to grey. The smaller the resulting particles, the darker the solution. The reaction was removed from the heat source and stirred at room temperature for one hour. Vacuum was applied to the solution to remove dimethylethylamine. The particles were then cleaned with centrifugation and sonication in dry THF to remove any unreacted alane, followed by three cycles in isopropanol. Isopropanol helps separate the particles from the capping agent. An oxide layer forms in this process that allows the particles to be stable for weeks (Figure 2). The particles were analyzed with X-ray photoelectron spectroscopy to confirm they are aluminum, and XPS-depth profiling demonstrates the particles are covered with an aluminum oxide layer (Figure 3).

Figure 2- HC-TEM images of aluminum nanocrystals washed in (A) THF, (B) IPA, and (C) Suspended in Isopropanol for 4 weeks. Scale bar = 200 nm.
Figure 3- XPS depth profiling of a pellet of synthesized aluminum nanocrystals. The aluminum was etched with an Ar$^+$ source at 3 kV over a 3 x 3 mm sample area. The etch rate was approximated as 0.25 nm/s from Ref. 4. The increasing Al$^0$ peak correlating with the loss of the Al$^{3+}$ peak with increasing etch time supports our picture of a nanocrystal geometry consisting of an alumina shell over an aluminum metal core. The persistence of the Al$^{3+}$ peak with further etch time is consistent with this geometry as well.

2.3. Results and Discussion

The ratio of THF and dioxane is vital in controlling the sizes of the aluminum nanocrystals obtained by this approach, however their precise role is elusive. We did not observe size or shape control when we varied capping agent concentration, which was also observed in organic phase synthesis of indium nanocrystals.$^{47}$ When toluene was substituted for dioxane (toluene has a similar viscosity to THF but a dielectric constant similar to dioxane) the resulting particles had the same size and shape as with the same ratio of THF/dioxane. These results suggest that particle size is more directly related to the dielectric properties of the solution and not to its viscosity.
Figure 4- Size control of aluminum nanocrystals. Increasing the fraction of tetrahydrafuran (THF) in a 1,4-dioxane/THF solution yields larger nanocrystals. a) Reaction scheme for synthesis of aluminum nanocrystals. b) Representative TEM images from synthesis with 0, 0.5, 0.6, and 0.8 THF volume fractions in a THF/1,4-dioxane solution (from left to right) (Scale bar = 100 nm).

Figure 5- Histograms for aluminum NC synthesized with different volume fractions of THF: 0 (black), 0.5 (red), 0.6 (green), and 0.8 (blue).

Histograms of the particles presented in Figure 3 were generated by measuring the sizes of 200 particles from each reaction of a given volume fraction (Figure 5). The size distributions corresponding to each volume fraction from Figure 1b (left to right) are, with the associated standard deviations, 55 ± 11 nm, 117 ± 11 nm, 152 ± 35 nm, and 223 ± 32 nm. A plot of nanocrystal size versus solvent ratio can
be found in the Appendix. Several shapes are present and we observed no change in the percentage of each shape for particles made with different fractions of THF. There are approximately 30% truncated trigonal bipyramids, 30% octahedra, 10% icosahedra, and the remaining 30% are mixed irregular crystals.

The optical properties of individual nanocrystals were obtained using a custom-built UV-visible dark field microscope (Figure 6). For the dark field measurements, a solution of aluminum nanocrystals was spin-coated onto a quartz substrate, and a scanning electron microscope (SEM) image of each nanocrystal was obtained following the measurement of its optical properties. The

![Figure 6 - Dark field spectroscopy of single aluminum nanocrystals. a) Experimental dark field spectra of 80, 120, 155 and 220 nm nanocrystals (top to bottom) (Scale bar = 100 nm). b) SEM images of respective particles. c) Theoretical calculation of spectra obtained using Mie theory, assuming spherical nanoparticles coated with a 3 nm oxide layer in a homogeneous dielectric environment.](image-url)
scattering spectrum of a series of nanocrystals of increasing size is shown in Figure 5a. In each case, the spectrum is dominated by the dipolar plasmon mode of the nanocrystal, which redshifts with increasing nanocrystal diameter. For nanocrystal sizes of 120 and 150 nm, we also observe a higher energy quadrupole mode at 5 and 4 eV, respectively. In this size range, the nanocrystal diameter is nearly half the size of the plasmon resonant wavelength, which results in significant optical phase retardation, increasing the magnitude of the higher order modes observed in the scattering spectrum. The SEM images in Figure 6b are particles corresponding to each spectrum in Figure 5a. A compilation of the dipolar and quadrupolar mode energies obtained from dark field scattering measurements of more individual nanocrystals is...
in Figure 6. Ensemble measurements do not retain the clear spectral response and we attribute this to the strong dependence of the plasmon resonance on nanocrystal size, not the shape polydispersity, which is not significantly large.

Figure 8- Comparison of the scattering cross section of an icosahedron of 155 nm diameter, obtained from a fully numerical solution of Maxwell’s equations (red curve) with the Mie theory calculations for a sphere of the same volume (black curve). Here we assume the particles to be in vacuum.

The experimental dark field spectra were compared with theoretical calculations obtained using Mie theory for similarly sized particles. Specifically, we model the aluminum nanoparticles as spheres coated by a 3 nm oxide layer with a diameter chosen to match the volume of the experimentally synthesized nanocrystals. As shown in Fig. 8, this approach produces scattering spectra that agree well with those obtained from a fully numerical simulation of Maxwell’s equations for the experimental geometry. Furthermore, we approximate the effect of the dielectric substrate by assuming a homogeneous environment with an effective dielectric
function equal to the average of the vacuum and substrate dielectric functions. Using the same illumination and collection conditions as in the experiment, we obtain theoretical spectra that agree remarkably well with the experimental measurements. Agreement between theory and experiment is best for smaller nanocrystal sizes; as their size increases, departure from spherical shape becomes more pronounced and the interaction with the substrate increases, effects not captured in this simple theoretical picture.

Cathodoluminescence (CL) was used to probe the local density of states of the nanocrystals, giving significant insight into the localization of the plasmon modes\textsuperscript{49} (Figure 9). For both sizes shown, the truncated bipyramids and icosahedra exhibit a 3-fold symmetric dipole response (Figure 9b). This is consistent with our theoretical simulations, shown in Figure 9c, where we calculate the far-field emission produced by the nanocrystals when excited by a single dipole placed at different positions on a plane 5 nm above the nanocrystal (simulating the electron excitation beam). These simulations were obtained by solving Maxwell’s equations using a finite difference time-domain numerical solver (Lumerical).
Figure 9- Cathodoluminescence images of the smallest and largest particles reveal similar charge density plots for varying sizes and shapes. a) SEM images of 70 and 155 nm icosahedra and 65 and 155 nm truncated trigonal bipyramids (right to left). b) Cathodoluminescence reveals a three-fold symmetry mode between 1.77 eV and 3.54 eV. c) Calculated cathodoluminescence images simulated using a single dipole excitation. Scale bar = 100 nm.

We also used scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) to characterize the Al nanocrystal plasmon modes (Figure 10); such techniques allow the identification and mapping of resonances with high spatial resolution. Strong plasmon resonances that were well-defined both spatially and spectrally were observed consistently in all single nanocrystals studied. STEM-EELS was performed on a monochromated, probe-corrected FEI Titan Themis operated at 200 kV and equipped with a Gatan Quantum ERS imaging filter; raw data from multiple beam positions are presented in Figure 10a. In the raw spectra, three
main features can be observed: the tail of the zero-loss peak decaying in intensity with increasing energy (all spectra), the low-loss intensity (2-8 eV) due to

![Figure 10](image-url)

**Figure 10** - Electron microscopy and spectroscopy of Al nanocrystals. a) Raw, low-loss, LSPR and Al bulk plasmon data of a 166 nm particle from the positions shown in the inset. b) EELS spectral components extracted by non-negative matrix factorization for the particle in (a). c) EELS maps representing the spatial distribution of the LSPR corresponding to the spectra in (b). d) core-loss EELS of a 166 nm Al nanocrystal at multiple positions showing the O-K peak (indicated by the arrow), and (inset) background-subtracted O-K intensity map. Scale bars = 50 nm.

LSPR interactions (surface positions), and the Al metal bulk plasmon at 14.9 eV (center of the particle). For the representative 165 nm diameter Al nanocrystal studied here, three prominent LSPR modes were found: the lowest energy at 3.3 eV and intermediate energy modes at 5.5 and 7.1 eV (Figure 10b). Plasmon maps (Figure 10c) were generated from plotting the contribution of each resonant mode, at each
pixel, for the modes (Figure 10b) extracted from the STEM-EELS data cube with non-negative matrix functionalization (performed in HYPERSPY). These maps consistently display 3-fold symmetry, corroborating the CL results. The field intensity for the lowest energy dipolar 3.3 eV plasmon mode (Figure 10c, top) is strongly localized at the tips of the particle, similar to the lower energy modes of a nanocube. The 5.5 eV mode (Figure 10b, center) is a quadrupolar LSPR with field intensity localized at the faces of the structure; analogies can again be made with the face mode of a nanocube. The 7.1 eV mode (Figure 10b, bottom) is also localized at the nanoparticle faces and is consistent with a higher order, octupolar plasmon mode.

STEM-EELS not only provides information on plasmon distribution, it can also characterize the elemental composition of the nanocrystal, through the oxygen-K (O-K) core-loss signal and Al bulk plasmon. Figure 10d shows core-loss EELS in the O-K region for multiple beam positions and the inset presents a map of the background-subtracted O-K intensity. The oxide layer fully surrounds the particle, albeit the O-K signal at the center of the particle is damped by multiple scattering (the thickness of the particle being ~165 nm) The thin oxide layer does not prevent efficient plasmon excitation, either in optical spectroscopy or electron-based techniques. EELS also reveals the particularly pronounced bulk plasmon of Al (Figure 10a). This very strong mode, observed around 14.9 eV, confirms the nanoparticle composition.
2.4. Conclusion

These uniform, robust, and air-stable nanocrystals are likely to be useful in many of the applications currently being pursued with gold and silver nanoparticles, including chemical sensing, surface-enhanced spectroscopies, and plasmonic materials and devices. In addition, they provide a far more sustainable alternative to gold and silver nanoparticles currently in widespread use, making them attractive for large-scale or large-area applications not considered practical previously, such as smart windows or displays, even paints and coatings. These new materials may replace organic pigments in applications where conditions such as long-term UV exposure may prove limiting to material lifetimes.
Manipulating Al Nanocrystal Growth through Solvent Complexation

Al nanocrystals are a cost-effective alternative to noble metal nanomaterials with their own unique plasmonic features throughout the UV, visible, and infrared spectrum. In the past two decades, generalized rules for nanocrystal growth have been established for noble metal nanocrystals, which can now be prepared in a large range of architectures, enabling the controlled synthesis of a variety of plasmonic nanostructures. In contrast, the synthesis of Al nanocrystals requires conditions where most surfactants and additives commonly utilized for nanoparticle size and shape control cannot be used. Here, we examine how the properties of Al nanocrystal growth-crystallinity, size and shape-can be influenced by interactions with solvent molecules. Ethers and amines coordinate to alane precursors, affecting crystallinity, size, and shape of the product nanocrystal in different ways. Ethers with multiple coordinating sites can polymerize precursor alanes, increasing the temperature necessary for their decomposition, ultimately resulting in smaller particles. Highly coordinated ethers and amines allow for predictably-shaped alane polymer
formation, allowing for samples with high size and shape homogeneity. These findings provide a basis for designing Al nanostructures through precursor control, and open the door for shape-controlled nanocrystals from air- and water-sensitive precursors.

### 3.1. Introduction

Advancements in synthesis and characterization have allowed unprecedented control of the size, shape, and composition of nanoscale materials. Many interesting optical, catalytic, and magnetic properties can now be accessed by manipulating nanomaterial architectures, allowing for a variety of applications ranging from anticancer agents to anti-counterfeiting materials. Coinage metals (Au, Ag, Cu) as well as Al can exhibit localized surface Plasmon resonance extinction maxima tunable throughout the UV, visible, and IR spectrum. Morphological control of noble metal nanocrystals has been widely studied, with factors such as seed crystal morphology, concentration, surfactants, ligands, reducing conditions, and halide additives pinpointed in their role in dictating size and shape. For example, the size of nanoparticles can be controlled by the concentration of seed nanocrystals in solution.

Al nanomaterials are a potentially low-cost alternative to noble metal nanocrystals with interesting plasmonic features. Although Al is highly susceptible to oxidation, Al nanocrystals form a 2-4 nm terminating layer of amorphous Al₂O₃ under ambient conditions that inhibit further oxidation. The
plasmonic features of Al nanocrystals make them interesting platforms for photocatalysis.\textsuperscript{67} Recent theoretical models suggest that Al@Al\textsubscript{2}O\textsubscript{3}-driven Pt photocatalysis should be more efficient than its Au-driven counterpart due to enhanced coupling.\textsuperscript{68} Crystalline Al is particularly promising for this application, since pristine Al has half the electron loss damping of conventionally-prepared high-defect Al materials.\textsuperscript{69} Al nanocrystals have been shown to be an efficient plasmonic photocatalyst for room temperature Hydrogen dissociation,\textsuperscript{67} and also to be useful as a nanoantenna, in combination with catalytic nanoparticles, in light-driven “antenna-reactor” designed complexes.\textsuperscript{70,71} Since small Al nanocrystals have localized surface plasmon resonances (LSPRs) in the UV, UV plasmonic photocatalysis is also possible. Al also offers a potentially interesting platform for surface-enhanced Raman spectroscopy (SERS).\textsuperscript{72} To make best use of the many useful properties of nanoscale Al, a better understanding of size and shape control is essential.

Recently we developed a robust, size-controlled chemical synthesis of Al nanocrystals through the decomposition of dimethylethylamine alane (DMEAA) with a Ti(IV) catalyst in an ethereal solvent.\textsuperscript{73} The conditions for this reaction stringently require the absence of any source of oxidation. For this reason, many common additives used to control shape in nanocrystalline syntheses, such as organic molecules containing hydroxides, carboxylic acids, halides, and nitrides, are incompatible with Al nanocrystal synthesis. Additionally, DMEAA decomposition proceeds rapidly, making shape control especially challenging. We demonstrated that size control is feasible through choice of solvent, where DMEAA decomposed in
tetrahydrofuran (THF) resulted in 220 nm nanocrystals while DMEAA decomposed in 1,4-dioxane resulted in 70 nm nanocrystals. Previous research on Al nanoparticle growth indicated the possible importance of the solvent. For example, the decomposition of LiAlH$_4$ in the presence of AlCl$_3$ was found to yield Al nanocrystals with sizes ranging from 100 nm to >1 μm.$^{23}$ When reactions were performed in ethereal solvents or in the presence of a strong Lewis base, particle size and size dispersity decreased.$^{26}$ However, the underlying rationale for solvent size control in this initial study had not been definitively determined.

In this paper, we report a systematic study of DMEAA decomposition in ethereal and aminated solvents, to more accurately determine how solvent selection and precise solvent mixtures direct Al nanocrystal growth. Infrared spectroscopic measurements supported by theoretical calculations of the Al-H stretching frequency of different alane complexes indicate that alane precursors coordinate to ethereal solvents. Lewis basicity of the ethereal solvent was found to control precursor formation. We found that solvents with multiple sites for alane coordination can induce alane-solvent polymerization, consistent with prior reports.$^{74}$ Polymerization can increase the decomposition temperature of the alane polymers, resulting in the formation of smaller particles.$^{38}$ Sample uniformity increases with the use of highly-coordinating ethereal solvents such as tetraglyme. These results indicate that control of Al nanocrystal shape and size is possible through precursor coordination, which can allow for a method for shape control similar to noble metal nanocrystals but
under the highly air and water-sensitive conditions required for Al nanocrystal growth.

3.2. Results and Discussion

![Figure 11 - Representative TEM images of Al nanocrystals prepared in various ethereal and amine solvents. The solvents and average particle sizes are a) trimethylamine (300-400 nm), b) N,N,N',N'-tetramethylethylene diamine (53 ± 12), c) N-methylmorpholine (92 ± 9nm), d) THF (141 ± 12 nm), e) dioxane (55 ± 12 nm) and f) toluene. Scale bars are 100 nm.](image)

The synthesis of Al nanocrystals requires air- and water-free techniques. In general, DMEAA is mixed with a compatible solvent followed by addition of the Ti(IV) catalyst Ti(OrPr)₄. Upon addition of the catalyst there is an expulsion of hydrogen gas,
Figure 12- Example of TEM measurements revealing twinning of Al NCs. a) In this sample from an MMOPRH reaction, several shapes are highlighted: truncated bipyramids (blue), pentagonally twinned NCs (green), octahedral (pink), and singly twinned beams (red). b) Using the top-down 2D views of different NCs, we can approximate the percentage of twinned particles in a sample to generate histograms describing c) size and d) shape.
as Al nanocrystals form. Previously we achieved nanocrystal size control by varying the ratios of different ethereal solvents. In this work, we chose a range of solvents that are compatible with our alane precursor for the Al nanocrystal reaction (Fig. 11). For each sample, we measured the size distribution of the Al nanocrystals using (> 100 particles per sample) transmission electron microscopy (TEM) (Fig. 11). Additionally, we determined twinning percentages by counting particle shapes that we observed in HR-TEM to contain twin defects, notably: singly crystalline octahedral and cuboctahedra, singly twinned beams and bipyramids, and pentagonally twinned nanocrystals (Fig. 12). Al nanocrystals synthesized in triethylamine ranged in size from 200 to 400 nm and the primary shape was octahedral. (TEA) (Fig. 11A). We chose TEA instead of dimethylamine (DMEA) because it has a boiling point above our reaction temperature (40°C). In our previous study, we noted that nanocrystals synthesized in dioxane were smaller than those synthesized in THF. To draw a clear comparison between the functional groups of ethers and tertiary amines with resulting nanocrystal size and shape, we synthesized Al nanocrystals in N,N,N’,N’-tetramethylenediamine (TMEDA), which is analogous to dioxane in its number of coordinating atoms (Fig. 11B). The resulting nanocrystals were small (53 nm in diameter) and contained a large fraction of singly and pentagonally twinned nanocrystals. We also synthesized Al nanocrystals in N-methylmorpholine (MMOPRH), which contains both an ether and a tertiary amine, resulting in Al nanocrystals that were 90 ± 9 nm in diameter. Additional TEM images for reactions in TMEDA and MMORPH are presented in Figure S2. We compared these results to Al nanocrystals synthesized in THF (Fig. 11D) and dioxane (Fig. 11E) synthesized as we
previously reported. Nanocrystals synthesized in THF were $141 \pm 12$ nm while nanocrystals synthesized in dioxane were $55 \pm 12$ nm. Al nanocrystals synthesized in the absence of a coordinating solvent, toluene (Fig.1F), yielded polydisperse nanocrystals with approximately a 60% standard deviation in size. Notably, the size of the nanocrystal was not dependent upon the type of functional group but on the number of coordination sites of the ethereal or aminated solvent. If the solvents have two coordination sites, then the resulting nanoparticles are small (below 100 nm in diameter). Additionally, amine-containing solvents yield a higher percentage of pentagonally twinned nanocrystals (a summary of these findings is in Table 2). Reactions in single coordinating solvents such as TEA, THF, trioctylamine, and dioctyl ether form nanocrystals larger than 150 nm in diameter. These results are consistent with our prior work in controlling Al nanocrystal size. Overall, size analyses indicate that doubly-coordinated solvent species results in smaller nanoparticle sizes.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Diameter (nm)</th>
<th>% Single Crystalline</th>
<th>% Singly Twinned</th>
<th>% Pentagonally Twinned</th>
</tr>
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<tbody>
<tr>
<td>THF</td>
<td>141 ± 12</td>
<td>39</td>
<td>56</td>
<td>3</td>
</tr>
<tr>
<td>DIOX</td>
<td>53 ± 6</td>
<td>21</td>
<td>74</td>
<td>4</td>
</tr>
<tr>
<td>TMEDA</td>
<td>53 ± 12</td>
<td>12</td>
<td>64</td>
<td>24</td>
</tr>
<tr>
<td>MMORPH</td>
<td>92 ± 9</td>
<td>23</td>
<td>62</td>
<td>15</td>
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Table 2- Compilation of diameters and crystallinity descriptions of nanocrystals for THF, DIOX, TMEDA, and MMORPH reaction

Aluminum hydride-adduct species exhibit a broad range of physical properties (melting point, decomposition temperature) and geometries that are dependent on the Lewis basicity, coordination and steric hindrance of the ligand. Generally, alane-adduct species are more stable with increasing Lewis basicity. This trend holds true
for single coordinating amines and ethers: a 2:1 THF:AlH₃ complex is unstable and decomposes into AlH₃ at room temperature, while a more volatile molecule, such as DMEA, forms a complex with alane that decomposes above 130°C. However, although dioxane is a weaker Lewis base than THF and DMEA, a DIOX:AlH₃ complex has almost the same decomposition temperature as the DMEA complex (125°C). The increased stability is attributed to the ability of dioxane to form polymeric alanes.

To understand how solvent coordination dictates the size and shape of Al nanocrystals, we monitored precursor complexation by FT-IR spectroscopy in the 1900-1600 cm⁻¹ region, where the Al-H stretching frequency occurs under various solvent conditions (Fig. 13). In each experiment, a 2:1 (ligand:AlH₃) stoichiometric amount of ligand was added to a solution of DMEAA in toluene (Fig. 13A). After the solution was stirred for 15 minutes, an FTIR spectrum was recorded. The spectrum was compared to known values for the Al-H stretching frequency of alane-ligand complexes as well as additional calculated spectra of THF, DIOX, and TMEDA:AlH₃ complexes. All theoretical calculations were performed using Gaussian 09. Global geometry optimization at the density functional theory (DFT) level was performed and the infrared spectra were calculated. We used the hybrid B3LYP functional and the 6-31+G(d) basis set consisting of a valence double-ζ basis set complemented with s and p diffuse functions, as well as d polarization functions for the carbon atoms.
Figure 13- FT-IR spectrum of Al nanocrystal reactions with resulting TEM image. a) Schematic of DMEA and ligand reactions. (left) Reaction ligand and (middle) experimental FT-IR of DMEAA in toluene (black) and in toluene with 2:1 ligand:alane amount of ligand (colored), and stick spectra of calculated Al-H vibration frequencies for DMEAA (black) and 2:1 ligand:alane. (right) TEM image of nanocrystal reaction in toluene with a 2:1 ligand:alane amount of b) THF, c) dioxane, and d) TMEDA. Scale bars are 100 nm.

DMEAA exhibits two distinct Al-H stretching frequencies at 1708 cm⁻¹ and 1777 cm⁻¹, corresponding to 2:1 and 1:1 DMEA:AlH₃ complexes, respectively. When only a 2:1 stoichiometric ratio of THF (Fig. 13B) or dioxane (Fig. 13C) is added, the
Al-H stretch peak positions in the DMEAA IR spectrum remain at 1708 cm\(^{-1}\) and 1777 cm\(^{-1}\). These spectra are in great contrast to the FTIR spectrum of DMEAA in the respective bulk solvents, which shows a strong feature at 1734 cm\(^{-1}\) arising from the Al-H stretch of the DMEA:AlH\(_3\):ether complex (Fig. 14). The resulting nanocrystals are 32 ± 12 nm and 37 ± 11 nm for THF and dioxane respectively, and exhibit poorly defined edges and sphere-like shapes (Fig. 13B, C). When DMEAA is mixed with an ethereal solvent, a peak in the IR spectrum at 1735 cm\(^{-1}\) appears, which can be attributed to an alane coordinated to both an ether and an amine; we do not observe this peak when using a stoichiometric ratio of dioxane or THF to DMEAA. When a stoichiometric amount of TMEDA was added to DMEAA in toluene (Fig. 13D) the 1:1 IR Al-H stretch typically observed at 1777 cm\(^{-1}\) was almost completely absent,
indicating that the alane had coordinated to the added amine. This reaction required more than 12h to complete at 40°C, far longer than the typical reaction completion time of 2 hours in other solvent combinations.

Figure 15- FTIR and TEM study of alane complexation with THF and resulting nanocrystal sizes. (Top) Representative TEM images of Al NCs synthesized in toluene and THF with THF volume fractions (left to right) 0%, 10%, 25%, 50%, and 85%. (Left) FTIR measurements of DMEAA in varying toluene/THF solutions. (Right) Area of ether-alane-amine peak versus total area of alane peaks plotted versus average diameter with error bars showing standard deviation. Scale bars are 200 nm.

We attribute this slowing of reaction kinetics to alane coordination with only TMEDA, which forms a complex more stable with alane than DMEA. We observed a similar effect on the rate of reactions with MMOPRH. While this complex cannot be
corroborated by IR spectroscopy since the Al-H stretch of (DMEA)$_2$:AlH$_3$ overlaps with (TMEDA)$_2$:AlH$_3$, TEM images indicate the nanocrystals synthesized with TMEDA were faceted crystals, predominantly singly twinned nanocrystals with a diameter of 39 ± 12 nm (Fig. 13D).

IR spectroscopy of the precursors also indicates a difference in precursor formation when THF is used as the solvent compared to toluene. A stretch at 1735 cm$^{-1}$ (Fig. 15) is present in the IR spectrum when DMEAA is solvated in THF, but is not present when DMEAA is solvated in toluene; we attribute this 1735 cm$^{-1}$ Al-H stretch to the formation of a DMEA:AlH$_3$:THF complex. To better understand the correlation between IR spectral features and nanoparticle size, we monitored the IR spectrum of alane for a range of THF/toluene ratios and characterized the product nanocrystals. We found that a coordinating solvent is essential to achieve a nanoparticle size distribution under 30%. At a 10% THF volume fraction, the 1735 cm$^{-1}$ Al-H stretching mode is clearly visible and the resulting nanocrystals have easily observable facets, differing from the same reaction when only a stoichiometric amount of THF was present. The resulting nanocrystals were 64 nm in diameter. At a 25% THF volume fraction, 90% of both the 1708 cm$^{-1}$ peak for (DMEA)$_2$:AlH$_3$ and the 1777 cm$^{-1}$ feature for DMEA:AlH$_3$ disappear and are replaced by the 1735 cm$^{-1}$ peak. Nanocrystals synthesized under these conditions are approximately 120 nm in diameter. At 50% THF volume, the 2:1 DMEA:AlH$_3$ peak is no longer observable, and the 1:1 peak is greatly diminished. The resulting nanocrystals are greater than 200 nm in diameter: this size does not increase with additional THF. For these reasons,
Figure 16- FTIR and TEM study of dioxane complexation with DMEAA and resulting nanocrystals. a) Ligand exchange of DMEAA with dioxane. b) FTIR measurements of DMEAA in (top to bottom) toluene, dioxane, and dioxane after a 3 hour reflux at 100°C with respective TEM images in c), d), and e). Stick spectra in the bottom (b) are computed infrared spectra. Color corresponds to the same color for frames in (a). Scale bars are 100 nm.
we believe that the increase in the Al-H stretch peak of THF:AlH₃:DMEA complex correlates with increasing nanocrystal size, but only under solvent conditions when there is less than a nominal 25% volume of THF. This cutoff point indicates that increasing particle size does not originate from the changing dielectric environment of the solvent. This observation corroborates with our hypothesis that ethereal solvents coordinate with alane precursors to dictate shape.

To further understand the trend of ether coordination with alane precursor and the effect on nanocrystal shape, we examined the FT-IR spectra of DMEAA in dioxane and the morphology of the resulting Al nanocrystals through TEM imaging (Fig. 16). Similar to THF, a peak emerges between the 2:1 and 1:1 DMEA:AlH₃ Al-H stretch features at 1708 and 1777 cm⁻¹, respectively. The location of this stretching mode is close in energy to the calculated vibrational mode energy for (DIOX)₂:AlH₃ and DMEA:AlH₃:DIOX. In the THF reactions, a 25% volume fraction of THF was sufficient to complex nearly all (DMEA)₂:AlH₃ into DMEA:AlH₃:THF. However, even with a 75% volume fraction of dioxane, the 2:1 DMEA:AlH₃ feature at 1708 cm⁻¹ is still prominent, indicating that dioxane binds weakly to the alane compared to THF, consistent with reported calculated values for the free energies of THF:AlH₃ versus DIOX:AlH₃.³⁵ Nanocrystals prepared with dioxane as a solvent are 55 ± 12 nm and exhibit a large shape distribution. Lewis Base-alane complexes can completely exchange ligands with a coordinating solvent under vacuum and/or heat.⁷⁷ Since DMEA is a relatively volatile ligand and dioxane is a relatively nonvolatile coordinating ligand, we expect dioxane to replace DMEA while DMEAA is stirred with
heat and under vacuum or dynamic inert-gas flow. We transaminated the alane species using a standard protocol by heating a solution of DMEAA in dioxane for 24h at 55°C to drive formation of only the (DIOX)$_2$:AlH$_3$ complex. After cooling to 40°C, analysis of the solution with FT-IR revealed a substantial decrease in the 2:1 DMEA:AlH$_3$ species indicated by the diminishing stretch at 1708 cm$^{-1}$: an appearance of the stretching mode at 1777 cm$^{-1}$ indicated an increasing concentration of the 1:1 complex. These results indicate that dioxane can replace a second DMEA species coordinated to the alane, but not to the first amine. Heating the reaction at 95°C for 3 hours increased the size of the DMEA:AlH$_3$:DIOX peak, but the DMEA:AlH$_3$ peak at 1778 cm$^{-1}$ remained present. TEM analysis indicated more regular nanocrystal shapes (Fig. 16). These results, together with our observations of increasing particle sizes and shape homogeneity with greater coordination of DMEAA with THF shown in Fig. 16, indicate that creating an alane complex with a less volatile ligand increases the expression of faceted crystals such as cuboctahedra and bipyramids. However, the concentration of the ethereal solvent must be high before it will exchange with a tertiary amine.
Figure 17- Representative TEM images of Al NCs synthesized in dioxane and THF with and without equivalent moles of DMEAA and TMEDA. A) Reaction of DMEAA with TMEDA to form a TMEDA-alane complex. B) FT-IR spectrum of DMEAA before (black) and after (red) addition of TMEDA including calculated Al-H stretches frequencies for alane complexes. TEM images of Al nanocrystals synthesized without TMEDA in C) dioxane (53 ± 6 nm) and D) THF (139 ± 17 nm), and with TMEDA in E) dioxane (47 ± 8 nm) and F) THF (67 ± 13 nm). Scale bars are 100 nm.
Figure 18- Additional TEM images of Al NCs synthesized with dioxane (top, scale bar = 100 nm) and THF (bottom, scale bar = 200 nm) as solvents.
Figure 19- Additional TEM images of Al NCs synthesized with added in TMEDA. Additional TMEDA with (top) dioxane and (bottom) THF as solvents. Scale bars are 100 nm.

From the FTIR experiments, we determined that the formation of alane complexes with coordinating solvents other than DMEA resulted in homogeneous
nanocrystals. While a high concentration of ethereal solvents is required for ligand exchange with DMEAA, only a stoichiometric amount of TMEDA is needed. We believe that if we form the TMEDA:AlH₃ complex in ethereal solvents, we should see only nanocrystals between 50-70 nm with increased twinning. We added a stoichiometric amount of TMEDA to DMEAA in THF and dioxane (Fig. 17A). The FTIR spectrum of both solutions showed a decrease in the 1778 cm⁻¹ Al-H stretch and an increase in the 1708 cm⁻¹ peak indicating the TMEDA complexed with the alane (Fig. 17B). Therefore, Al NC reactions in these conditions will only have alanes coordinated with a multicoordinating ligand.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Diameter (nm)</th>
<th>% Single Crystal</th>
<th>% Singly Twinned</th>
<th>% Pentagonally Twinned</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF + TMEDA</td>
<td>67 ± 13</td>
<td>22</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>DIOX + TMEDA</td>
<td>47 ± 8</td>
<td>12</td>
<td>67</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 3- Compilation of diameters and crystallinity descriptions of nanocrystals for THF and DIOX reactions with stoichiometric additions of TMEDA.

Because the addition of TMEDA greatly increases the reaction time at 40°C from 1.5h to approximately 12h, we increased the oil bath temperature to 60°C for these reactions. Control Al NC reactions in dioxane (Fig. 16C) and THF (Fig. 17D) were carried out at this temperature and the resulting particles are similarly sized relative to what was observed at 40°C in Figure 1. The Al NC reaction with added TMEDA in dioxane yielded more twinned nanocrystals (Fig. 17E) while the similar Al NC reaction in THF yielded nanocrystals with an average diameter of 63 ± 13 nm (Fig. 17F). Additional TEM images of the control reactions are present in Figure 17 and for
TMEDA reactions in Figure 18. The presence of TMEDA significantly increased the number of twinned nanocrystals in both reactions while also decreasing the size of nanocrystals in THF (Table 3). These results further indicate that alane precursors determine nanoparticle size and morphology and the relative basicity of the ligands needs to be considered when choosing a solvent for an Al NC reaction.

![TEM images of Al nanocrystals synthesized in different solvents](image)

**Figure 20- Size and shape analysis of Al nanocrystals synthesized in different linear ethereal solvents.** Representative TEM images of nanocrystals synthesized in a) glyme (153 ±24 nm), b) diglyme (105 ± 12 nm), c) triglyme (102 ± 13 nm), and d) tetraglyme (164 ± 36 nm). Scale bars are 100 nm.

To further understand the relationship between the number of coordination sites and size, we decomposed DMEAA in linear-chain solvents with 2, 3, 4, and 5 ethereal coordination sites. TEM images of nanocrystals synthesized in increasing
lengths of linear ethers are shown in Figure 20. The primary shapes observed in each of these reactions are single crystalline octahedra and cuboctahedra, and singly twinned nanocrystals. We observed variations in the size and shape of nanocrystals prepared in all of these solvents. Nanocrystals prepared in glyme were 152 ± 23 nm and we observed a wide range of structures with varying twinning defects (Fig. 20A). In diglyme (Fig. 20B) and triglyme (Fig. 20C) we observed smaller nanocrystals with average diameters of 105 ± 12 nm and 103 ± 10 nm respectively. However, in tetr glyme the average diameter of Al nanocrystals increased to 164 ± 36 nm (Fig. 20D). Overall, we observed an increase in singly crystalline nanocrystals with increasing ether chain length (See appendix for additional TEM images) and have summarized our studies on the

<table>
<thead>
<tr>
<th>Solvent</th>
<th>% Single crystalline</th>
<th>% Twinned</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyme</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>Diglyme</td>
<td>38</td>
<td>58</td>
</tr>
<tr>
<td>Triglyme</td>
<td>50</td>
<td>46</td>
</tr>
<tr>
<td>Tetr glyme</td>
<td>54</td>
<td>45</td>
</tr>
</tbody>
</table>

**Table 4- Compilation of diameters and crystallinity descriptions of nanocrystals synthesized in linear ethereal solvents.**

degree of twinning in Table 4. We attribute the increasing shape uniformity to a decreasing steric hinderance of the alane-coordinating oxygens\(^{31}\) with increasing chain length. Therefore, additional coordination sites allow for a more uniform pre-arrangement of alane precursors in solution before decomposition, forming more uniform structures, but only if the coordination sites are not sterically hindered.\(^{34}\) However, decomposing DMEAA with a highly-coordinating amine, \(N,N,N',N''\)-
pentamethyldiethylenetriamine (3 N’s) and 1,1,4,6,10,10-
hexamethyltriethylenetetramine (4 N’s) yields a polydisperse, single crystalline and
twinned sample with sizes between 60-70 nm (Fig. 21) indicating that this trend of
increasing monodispersity with the number of coordination sites may not apply to
aminated solvents.

**Figure 21-** Representative TEM images of Al NCs synthesized with a) PMDTA and
b) HMTETA as solvents with average sizes of 67 ± 8 nm and 56 ± 15 nm
respectively. Scale bars are 50 nm.

### 3.3. Conclusion

Control of the growth of Al nanocrystals is uniquely challenging due to the
immense sensitivity of alane precursors, which limits the use of capping agents. Even
so, we found similarly sized Al nanocrystals are achievable through control of the
solvent. IR spectroscopic studies indicate that both ethereal and aminated
coordination can alter the arrangement of the Al precursor prior to its decomposition, dictating the nucleation and growth of the resulting nanocrystals. Specifically, we observed that alanes coordinated with dual coordinating tertiary amines and ethereal solvents yield sub 100 nm nanocrystals, while similar single coordinating solvents yield nanocrystals with diameters above 150 nm. Additionally, the presence of a dual coordinating solvent with a tertiary amine increased the amount of pentagonally twinned nanocrystals. Although the size trends did not extend to linear chain ethers with more coordination sites, we did observe an increase in the number of single crystalline nanocrystals. These observations provide a rationale for what influences the early steps of Al nanocrystal growth, and provide initial insight towards a roadmap for engineering this cost-effective and highly interesting material to a wide variety of nanocrystalline architectures.
Chapter 4

Summary

This work has investigated the wet chemical synthesis of aluminum nanocrystals and developed criteria for the shape and size control. Specifically, rational design of aluminum nanocrystals from an alane precursor requires understanding of the coordination chemistry of alanes.

The Al nanocrystal reaction does not require the traditional capping agents in other metal nanocrystal growth syntheses, such as carboxylic acids, if the reactions are carried out in a coordinating solvent. The reactions in coordinating solvents are advantageous because many capping agents are difficult to remove and clean which will hinder TEM/SEM characterization. If a capping agent is used, the ratio of capping agent to alane precursor should remain below 1:3 so the alane does not react with the capping agent to form a stable complex of $L\cdot\text{AlH}_3\cdot L'$. 

Alanes are compatible with a few function groups and among those are ethers, thioethers, tertiary amines, tertiary phosphines which can coordinate with alane. Coordination of the alane will lead to different physical properties such as increased or decreased stability. Whether or not the coordination is desirable, a
researcher must understand and consider the relative basicity and steric of solvents containing these function groups as alanes are prone to ligand exchange, especially under vacuum and heating. This work showed that strong Lewis Base, multi-coordinating amines led to a higher degree of twinned nanocrystals and smaller nanocrystals, even if the amount of added amine was equivalent to the amount of alane.
References


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Appendix A

Figure A-1- Plot of average diameter of particles from synthesis with various volume fraction of THF/THF + dioxane. Standard deviations on measurements are shown for each volume fraction.

Figure A-2 a) EELS spectral components from an Al NC. b) EELS maps representing the spatial distribution of the LSPR corresponding to the spectra in (a). This is similar to what is shown in Figure 4 in the manuscript.
Figure A-3. EELS spectral components extracted from non-negative matrix factorization of raw EELS spectra at each position indicated by the point on the inset.
Figure A-4. Additional representative TEM images of Al NCs synthesized with linear chain ethers: (red) glyme, (blue) diglyme, (green) triglyme, and (magenta) tetraglyme. Scale bars are 100 nm.