RICE UNIVERSITY
Chemistry Mediated Mechanical Behavior of Inorganic Nanostructures

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
Doctor of Philosophy

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HOUSTON, TEXAS
August 2021
ABSTRACT

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Unique and fascinating chemistry transpires at surfaces that cannot take place in bulk materials due to the presence of dangling bonds as well as strained or otherwise unusual coordination environments. As the size of an object becomes smaller, the fraction of surface atoms to bulk atoms increases. Ultimately, for nanometer-sized particles, surface effects become so large that the behavior of the system can change completely, leading to many of the unique properties associated with nanoscale materials. At this length scale, forces that would ordinarily have little to no influence on atoms in the bulk can have an enormous impact on surface atoms and thus dictate the behavior of the system. Since all inorganic nanoparticles are capped with organic ligands that provide them stability in solution, the chemistry at the surface atom-ligand interface can be leveraged to drive new chemical processes or physical phenomena that would be impossible at any other length scale.

Colloidal silver nanoplates can be readily synthesized that are several nanometers thin, maximizing the fraction of surface atoms and making them an ideal candidate for studying the effects of surface chemistry on nanoparticle properties. Their high aspect ratio renders them unusually flexible such that when draped over much small spherical nanoparticles, the plates deform, a process that can be observed via distinctive bend contours in electron microscopy images. Topographically, this locally deformed region presents as an axially symmetric bump on the surface of the nanoplate, as confirmed by atomic force microscopy measurements. To understand the structural nature of this deformation, an
analytical model based on Kirchhoff-Love plate theory was developed. This reveals that the local deformation of the nanoplate around the spherical particle is driven by the Van der Waals (VdW) interaction between the nanoplate and the experimental substrate. The ability for the VdW interaction to deform the nanoplate is shown to be heavily dependent on the thickness of the nanoplate; and it is estimated that structures thicker than ~10 nm would not be deformable. For the experimentally observed deformation to be possible, the analytical model must include plastic deformation, the occurrence of which was further confirmed by finite element simulations (COMSOL) as well as electron microscopy studies.

The size of the described bend contour is related to the extent of the topographical deformation in the nanoplate. This was confirmed by varying the size of the sphere over which the nanoplate was deformed, displaying that the size of the bend contour was directly related to the size of the spherical nanoparticle. With this in mind, we hypothesized that the bend contours could be used to study the potential influence of surface chemistry on mechanical properties. As synthesized, the nanoplates are capped with a weakly bound citrate ligand which can be replaced with a library of other commonly used molecules: pyrrolidone (PVP), a phosphine, a thiol, and an N-heterocyclic carbene. It was found that the spatial extent of the bend contour changed proportionally to the binding strength of the surface ligand, suggesting that the mechanical strength of the nanoplate is also proportionally related to binding strength. We postulate that this mechano-chemical coupling arises from the atomic reorganization of surface atoms upon interactions with increasingly strongly binding ligands, changing the surface stress and the yield strength. In the case of more strongly binding ligands, the atomic reorganization of the surface layers of atoms is so severe that the nanoplate becomes stronger and the extent of the spatial deformation is larger than for weaker bound ligands. This work investigates a fundamentally new size-dependent interaction driven by the surface chemistry of inorganic nanoparticles. We envision using
these results as a basis for being able to create a new class of nanoscale materials capable of physical bending and structurally reconfiguring themselves via chemical cues to adapt to the needs of a given application.
Acknowledgments

Throughout my time in graduate school at Rice I have always felt fortunate to be surrounded by incredible people who have made me better in a variety of ways. Here, I hope to mention them all and thank them for their roles in supporting me and this work.

First, I would like to thank my academic advisor, Professor Matthew Jones. Joining his research group was perhaps the best decision I made in my graduate career. He has been an amazing mentor, and it has been my honor to be one of the first graduate students to have the privilege of working with him as an advisor. He has always been encouraging and instructive, providing his own scientific insight and advice, when necessary, but has largely allowed me to operate in a highly self-directed manner. I have treasured the hours of conversations we have had trying to understand the intricacies of a research topic that neither of us started out being acquainted with. I admire his investigative and fundamental approach to scientific research and his incredible ability to communicate science. I only hope that a fraction of those skills has rubbed off onto me. Perhaps the most important lesson of all that Matt has taught me is how awful the font Calibri truly is.

I must also thank my other committee members, Professors Angel Martí, Ken Whitmire, and Geoff Wehmeyer. The former two provided valuable feedback during my qualifying exam that has only improved my research in the latter half of my graduate work. The latter offered good discussion as well as simulation results that contributed greatly to the work discussed in Chapter 2.
The Jones lab members have been a great group of people to work alongside, and I am grateful to them all for the intellectual and emotional support that they have provided to me over the years. I’d like to especially thank Theo Gerrard-Anderson for his onerous work in providing mathematical derivations that have greatly supplemented my experimental work; without his effort this thesis would have suffered greatly. I can only imagine the amount of time and effort he has spent building mechanical models from the ground up and generating/re-generating many graphs for me when I asked for the parameters, color schemes, and scaling to be changed. I’m particularly grateful for my original labmates Rachael Kress and David Marolf who started this journey in the Jones Lab with me. They were great teammates as we all figured out how to operate in the early stages of our research group. We undertook many tasks together, not the least of which was trying to surreptitiously shorten our group meetings, an undertaking we failed at miserably. I’ll always remember the traditions of the lab that we started that I hope continue on for many years to come. Additionally, I thank my mentee, Tim Robertson, for making me look good by being a quick learner and a reliable experimentalist. I can’t wait to see what you’ll accomplish in the years to come. Finally, I want to express my general gratitude for the other members of the Jones Lab: Liang Qiao, Arzeena Ali, Muhua Sun, Zhihua Cheng, Zhi Yang, and Carly Graverson.

I would also like to express my appreciation for the Rice Chemistry Department as well as the Chemistry Graduate Student Association who have provided a supportive and enjoyable working environment, where there is always someone to lend a helping hand when needed. Additionally, I’d like to acknowledge
the Rice Shared Equipment Authority for providing and maintaining the equipment and instrumental facilities that I utilized to conduct my research.

Although I always had an innate interest in the sciences, I would not be here today if it weren't for many exemplary educators that encouraged me along the way. Diane Williams was perhaps the first teacher who truly helped me to believe in myself and my own abilities, and for that I will never be able to thank her enough. Seventh grade science, taught by Pam Starry, and high school chemistry, taught by Carol Foss, were classes that confirmed my love for the physical sciences and kept me on an advanced educational track in the sciences. I’d also like to express my utmost gratitude for the entire Chemistry Department at Boise State University for the exemplary education they provided to me that aided in my later successes. In particular, I want to recognize Dr. Henry Charlier Jr. as well as Dr. Jeunghoon Lee for being incredible undergraduate research mentors. It is only through their belief in me and support of me that I have come so far. Lastly, I want to thank the Honors College at Boise State University for providing an invaluable academic community that I learned so much from and had a so much fun being a part of. Special thanks to Dr. Andrew Finstuen for facilitating my intellectual curiosity outside of the sciences as well as teaching me how to write like a historian.

Lastly, I’d like to thank my family, both immediate and extended, for all their support while I have undertaken this massive endeavor. My parents, Steve and Liz Rehn, have always encouraged me in all of my ambitions and sacrificed more than I’ll probably ever realize to do so. I feel very fortunate to have parents that are interested
and engaged in what I do. I want to thank my brother, Kris Rehn, for always being there to talk to when I need it. Part of what has gotten me through this process is knowing that you were rooting for me. I also want to thank my aunt, Roxanne Marshall, and my cousin, who is like a sister to me, Jenny Busby. Both of you have always been excited about my educational ambitions and have introduced me to one of my life's greatest passions, good wine. The family I have gained along the way in graduate school has had probably the largest positive impact on me and has been my constant source of encouragement. Lauren, thank you for being my best friend; we've laughed, cried, celebrated, commiserated, and grown up together in these last five years. I can’t wait for all of the memories we’ll make in the future. Finally, I want to thank my amazing husband, Marc Thompson, who has picked me up and dusted me off after long days at the lab or experiments gone wrong and cheered with me after each and every achievement, small or large. I could not have asked for a better spouse and I’m so grateful to have you in my life.

To Jack, thank you for seeing me through as much as you could. I miss you every day and I hope that you are happy wherever you are.
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BCC</td>
<td>Body-Centered Cubic</td>
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<tr>
<td>BF</td>
<td>Bright Field</td>
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<tr>
<td>BSPP</td>
<td>Bis(p-sulfonatophenyl)phenylphosphine</td>
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<tr>
<td>DF</td>
<td>Dark Field</td>
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<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
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<tr>
<td>DOS</td>
<td>Density of States</td>
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<tr>
<td>FCC</td>
<td>Face-Centered Cubic</td>
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<tr>
<td>FEM</td>
<td>Finite Element Method</td>
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<tr>
<td>FFT</td>
<td>Fast-Fourier Transform</td>
</tr>
<tr>
<td>HAADF</td>
<td>High Angle Annular Dark Field</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal-Close Packed</td>
</tr>
<tr>
<td>HR</td>
<td>High Resolution</td>
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<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic Liquid</td>
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<tr>
<td>LEED</td>
<td>Low-Energy Electron Diffraction</td>
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<tr>
<td>LP</td>
<td>Liquid-Phase</td>
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<tr>
<td>LSPR</td>
<td>Localized-Surface Plasmon Resonance</td>
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<tr>
<td>MO</td>
<td>Molecular Orbital</td>
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<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>-------------</td>
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<tr>
<td>NHC</td>
<td>N-Heterocyclic Carbene</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene Glycol</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum Dot</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected-Area Electron Diffraction</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-Assembled Monolayer</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid-Electrolyte Interphase</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface-Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>TGA</td>
<td>Thermogravimetric Analysis</td>
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<td>THF</td>
<td>Tetrahydrofuran</td>
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Chapter 1

The Intricacies and Consequences of Molecular Adsorption at Metal Surfaces: Connecting Global Observables to Atomic Events

1.1. Abstract

For decades, the interactions between surfaces and atomic/molecular adsorbates have been studied extensively. From one perspective, adsorbate binding to one-sided metal cantilevers results in bending – a phenomenon attributed to the differential surface stress. However, due to the continuum-level understanding in this field, little is known about how differences in the chemical makeup of adsorbates affects cantilever deflection, and the atomic-level origins of surface stress. Conversely, traditional surface science has built a very in-depth understanding of the

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1 Material in this chapter will appear as a review article in a subsequent publication.
atomic restructuring that is induced when adsorbates bind to surfaces but does not relate these events to macroscale behavior/properties. Models used in the surface science literature to understand the relationship between adsorbate binding and surface stress do not account for important factors such as the band structure and density of states of the metal surface. Here, we review both areas of literature, highlighting advances as well as describing contradictions and knowledge gaps. We present a way to think about molecular adsorption at metal surfaces in terms of molecular orbital theory, a framework that can help provide a more accurate understanding of adsorbate binding with the aid of simulations for situation-specific knowledge. Finally, we discuss the promise of nanoscale materials as a length-scale bridge between cantilever and surface science literature to build an experimental multi-scale model for adsorbate binding to metal surfaces.

1.2. Introduction

Condensed matter states by necessity exhibit surfaces. This results in the existence of interfaces between matter of different compositions and/or states. These interfaces, due to their unnatural coordination and electronic environments, display extraordinary physical and chemical properties. For this reason, most important natural and technological processes involve interactions at surfaces and interfaces - so much so that surface science has emerged as a frontier area of research in many different subdisciplines: bio-interfaces, catalysis, and nanoscience.
In the past several decades, surface science has been in a stage of accelerated progress, mostly owing to the development of increasingly powerful structural and chemical characterization techniques (Figure 1-1). Whereas beforehand much of surface science was based on an empirical understanding from macroscale events, more recently surfaces can be characterized with angstrom-level precision. It is from this history that two distinct areas of research arise from in terms of the understanding of interactions at interfaces, perhaps the most general of which is adsorbate binding. From the macroscale perspective, adsorbate binding can modulate the intrinsic stresses present in a surface, which results in an observable, such as cantilever deflection.\textsuperscript{1} However, most of this work is based on a continuum mechanics framework with little acknowledgement for the nature of the atomic interactions at play. By contrast, sub-microscale surface studies involving techniques such as low-energy electron diffraction (LEED), focus almost exclusively on surface atom positioning and restructuring upon interaction with adsorbates, and do not study the global scale results of such events.\textsuperscript{2} Consequently, these two approaches study a similar phenomenon at incongruent length scales. It is one of the great endeavors of scientific research to establish a multi-scale understanding of natural phenomena. Therefore, it is of vital importance to connect observations from these two length scales into a cohesive paradigm, a problem to which nanoscale research presents a tractable solution.
Figure 1-1. A historical overview of surface science topics and advancements. It can be observed from this graphic that there is a clear progression from macro-scale properties and behavior to sub-microscale investigations as instrumentation has become more advanced. Reprinted with permission from ref 3.

As the size of an object decreases, its ratio of surface area to volume increases, meaning that there are more surface atoms relative to bulk atoms. For nano-sized structures, where this ratio is further heightened, properties associated with surface effects become dominant. When objects become even smaller, such as in the case of metal nanoclusters, every atom can be viewed as a surface atom. This trend marks nanoscale objects as an intermediate between atomic restructuring events at surfaces and the macroscale consequences of adsorption. For a nanoparticle, surface effects of
adsorbate binding can govern the behavior of a system, and thus allow for both atomic characterization and global-scale observations.

The aim of this review is to summarize and highlight research achievements from the macro-scale and the sub-microscale research areas concerning how adsorbate-metal surface interactions impact surface atomic organization, surface stress, and material properties. First, we will examine the relationship between surface stress and macroscale properties, a topic perhaps best appreciated by the molecular sensing literature in terms of cantilever deflection. Then, we will discuss what surface science has illuminated about the relationship between surface stress and atomic reorganization as well as the complexities of assessing the strength of bonding between an adsorbate and a surface - a parameter that is extremely important in approximating the amount of induced surface stress and atomic restructuring from a bottom-up approach. By understanding the progression of these two fields in parallel, we hope to reveal the gaps in knowledge that the two areas have that may be filled by converging. To conclude, ligand (adsorbate) mediated behavior in nanoparticles will be discussed, as the global effects of such interactions are becoming more appreciated in recent studies. We also, hope that by bringing these fields together, we will push them forward in an exciting new direction. Not only is there an opportunity for a multiscale understanding of adsorbate effects in the context of nanoscale structures, but these studies would have vast implications for inorganic nanoscience, where systems are particularly sensitive to these surface effects.
1.3. Defining the Surface

The area defined as the surface or interface in any give context is material dependent but is usually considered to be one to several atomic layers into a solid lattice. For instance, charging at the surface of an insulator can produce effects that extend hundreds of atomic layers into the material. By contrast, an organic molecule interacting with a metal surface can be described accurately by considering the properties of a monolayer of organic molecules and its effects on the two to four metal atomic layers beneath it. The traditional materials studied by the surface science community were bare, low Miller-index facets of fcc and bcc metals due to their simple structure and relative stability. Studies of the structures of adsorbed species to these surfaces were performed to understand their precise physics and chemistry as a platform for studying more complex surface behavior. Here, we discuss adsorption to low-index metallic surfaces – and as such will assume that any surface interaction will induce effects across a few atomic surface layers.\(^3\)\(^4\)

1.4. Macroscale Effects of Surface Stress – Cantilever Deflection

Surface stress describes the amount of work required to elastically stretch a surface. In the early 1900’s, G. G. Stoney observed that the radius of curvature of a thin metallic film was related to the stress intrinsic in the surface. From this observation, he developed a mathematical relationship between the two variables:\(^5\)
Equation 1-1. Stoney’s formula for the relationship between surface stress changes and the radius of curvature of a film.

\[ \Delta \tau_s = \frac{Et^2}{6R(1-v)} \]

where \( \Delta \tau_s \) is the change stress of a surface based on \( E, t, v, \) and \( R \) (Young’s modulus, thickness, Poisson ratio, and radius of curvature). This relationship is the basis for the massive amount of literature that investigates the deflection of cantilevers as a function of surface stress, particularly in the context of adsorbate-induced surface stress. It is important to note that this relationship and the concept of surface stress inherently fits under the paradigm of continuum mechanics, where objects are considered to be made up of a continuous mass, rather than discrete atoms.

Since Stoney’s foundational work, it has been further confirmed that surface stress and the deflection of thin films are directly related,\(^6\)-\(^{10}\) and it became obvious that cantilever-based deflection could be used as a molecular sensing tool for measuring the concentration of adsorbates when a work by D. Wolf suggested that surface stress induced by adsorbate binding is directly related to surface coverage.\(^{11,12}\) This work was followed by many published examples of employing cantilever-based deflection platforms for molecular and biological sensing as well as further work in understanding the fundamentals of adsorbate-induced surface stress.\(^{13-23}\) For example, Berger et al examined the surface stress induced by the assembly of alkanethiols on a gold-coated cantilever, a model system that would become
commonly used in the field and will be discussed further.\textsuperscript{24} Simultaneously, Antonik et al employed the cantilever platform to study interactions between biological cells.\textsuperscript{25}

In 1975, Lagowski et al reported that molecular adsorption on the surface of microcantilevers induced surface stresses (known to be as large as -16 N m\textsuperscript{-1}) that changed their natural resonance frequency, suggesting that adsorption led to a difference in the surface elastic properties.\textsuperscript{26} However, shortly thereafter, a separate study presented calculations demonstrating that changes in surface elasticity would have negligible effects on the resonance frequency. This second work, however, provided no alternative explanation for the phenomenon.\textsuperscript{27} Subsequent publications attributed the resonance frequency shifts to the mass loading of adsorbates as well as a change in the spring constant of the cantilever, a surface elasticity effect, despite the previous finding.\textsuperscript{28-35} Conversely, another host of studies published in the same time period suggested that mass loading is not a contributing factor.\textsuperscript{36-38} In addition to the lack of mechanistic understanding behind resonance frequency changes, a 2001 study revealed that there is a high level of uncertainty associated with the Young’s moduli of these fabricated cantilevers, and as such is not a good metric for understanding the behavior of a system.\textsuperscript{39} This example is just one where several studies conflict with one another in trying to determine the mechanisms behind the observed behavior of cantilevers upon molecular adsorption, suggesting that a macro-scale, continuum-based understanding is not sufficient for predicting the behavior of the system.
The interaction energy between surface molecules has been historically known to arise from a wide number of mechanisms, namely electrostatic repulsion, hydration forces, steric effects, van der Waals forces, and entropic interactions.\textsuperscript{40-43} Therefore, much work was put towards understanding how adsorbate-adsorbate interactions may affect the subsequent deflection behavior of cantilevers. For instance, studies were performed demonstrating differential deflection in the presence of a variety of alcohols.\textsuperscript{44} Additionally, one of the foundational studies during this time was published in 1998 by Berger et al, who reported that longer-chain alkanethiols increase the bending of cantilevers, hypothesizing that this is due to the variation in dipole moments between the adsorbates.\textsuperscript{45} Later work built on this observation posited that the main mechanism behind cantilever deflection via surface stress was indeed due to intermolecular interactions between immobilized adsorbates.\textsuperscript{15, 34, 46-50} However, a later study by M. Godin (2004) demonstrated experimentally that surface stress was independent of alkanethiol chain length for an atomically flat gold surface.\textsuperscript{51} Godin rebutted the work by Berger et al through computational and experimental evidence that demonstrated the well-known 30 degree tilt of close-packed alkanethiol monolayers due to van der Waals interactions would not be possible if there were a strong electrostatic repulsion.\textsuperscript{45, 51, 52} Furthermore, to explain the previously observed dependence on adsorbate interaction, Godin showed that the kinetics of adsorption and the final density of the alkanethiol monolayer is dependent upon the grain size of gold films. For larger grain size and lower surface roughness, monolayer formation progresses to completion to
form a close-packed, standing up configuration. This results in the maximal surface stress change. For smaller grain size and greater surface roughness, monolayer formation stops at a phase where the density is low, and alkanethiol molecules lay down on the gold surface, resulting in a much smaller surface stress change (0.5 N m\(^{-1}\)). Because cantilevers in these works are fabricated by gold evaporation, there is likely a strong variance in the crystalline quality of surface produced, affecting the packing behavior of adsorbates, and thus the induced surface stress. Shortly after Godin’s published work, studies by Desikan et al demonstrated that surface stresses were also dependent on the surrounding medium (vapor or solution) in addition to the crystallinity of the surface,\(^{53,54}\) and Mertens et al published results demonstrating that high surface roughness was related to more surface stress from molecular adsorption (a contradiction to Godin’s work).\(^{55}\) This collection of works, despite their incongruencies, explain that adsorbate-driven cantilever behavior is highly dependent on experimental conditions, such as surface grain size and the surrounding medium, the mechanistic consequences of which are not well understood.\(^{24,45,51,53-57}\) In fact, the underlying mechanisms behind the response of cantilevers to adsorbates was still extensively argued as of 2008.\(^{58}\)

In 2010, further work by Godin et al conducted molecular simulations that demonstrated that intermolecular adsorbate interactions and electrostatic forces were only capable of generating small surface stresses, and posited that surface charge redistribution was perhaps the principal factor in cantilever deflection.\(^{1,59}\) This explanation was consistent with their previous observation that side chain
interactions were not a factor in induced surface stress, and also countered previous hypotheses about the effects of the vast array of intermolecular interactions that could take place between surface-tethered adsorbates. Godin’s charge redistribution hypothesis validates an empirical relationship proposed in 1995 that suggested that the binding energy of an adsorbate and its induced surface stress are directly related. From this relationship, experiments have estimated the binding energies for adsorbates such as DNA-oligos. This connection between adsorbate binding strength and surface stress-driven deflection, was further validated in a relatively recent study by Pinnaduwage et al, where it was experimentally observed that the strength of the adsorbate interaction was directly related to the extent cantilever deflection (Figure 1-2). One of the adsorbates tested, hexene, interacted via weak physisorption with a gold cantilever surface, corresponding to the smallest deflection value of 200 nm. When molecules were allowed to associate with the cantilever via hydrogen bonding, a stronger interaction, the cantilever deflection increased to 1000 nm. Finally, when molecules covalently bonded to the surface of the cantilever, a very strong interaction, the largest extent of cantilever deflection was observed, 4000 nm. This in combination with previous studies and conclusions validated the direct relationship between adsorbate binding strength, surface stress, and the mechanical behavior of cantilevers.
Most recently, a study by Zhao et al verified Godin's work that inter- and intrachain interactions are not a significant contribution to surface stress change in a densely packed system, but suggested that the origin of surface stress from monolayer formation on a cantilever may be due to the surface reconstruction of the gold substrate, a factor that is closely related to interaction strength. Direct computational work predicted a surface stress range for increasing surface coverage of alkanethiols on gold to be 0.12-3.06 N m$^{-1}$ and the continuum elasticity-based computation provided a surface stress range of 0.16-4.38 N m$^{-1}$ - the two models predicting stresses of similar magnitude. These results are significant owing to the
fact that they are perhaps the only example of utilization of a multi-scale model to predict the behavior of surface stress-based cantilever deflection. However, even though an atomic-scale model is employed, the actual atomic-scale restructuring events are not discussed.

By its very nature, the interaction of a molecule with a surface is one that is rife with atomic-level minutiae. Therefore, it is unsurprising that there is still many knowledge gaps and contradictions in this area of the literature, due to the fact that the sub-microscale response of surface atoms to adsorbate binding is not considered. Because of this, a lone continuum-scale understanding can never completely predict the behavior of global-scale systems in response to adsorbate binding. It is necessary to understand the surface as a collection of atoms that responds in elaborate ways to interactions with other atomic and molecular species. Therefore, we will next look into how the classic surface science has worked towards an understanding of these intricacies.

1.5. Adsorbate-Induced Surface Atom Reorganization

When a surface is created, bonds between atoms must be sacrificed. As a result, atoms at a surface exist in a very different environment compared to the bulk. The electronic state of surface atoms is unfavorable and must be reorganized to its lowest energy configuration. One model to describe this is known as the backbonding model, where electronic charge at the surface will be redistributed amongst the
surface atoms and the atomic layer beneath, leading to an increase in charge density between these atoms. This also increases the interatomic cohesion and leads to the contraction commonly found in the topmost layers of bare metals, corresponding to an intrinsic tensile surface stress. The surface contraction for a bare (111) surface has been observed to be as much as 15%, depending on the roughness.65-67

In this way, surfaces maintain a stable formation and boundary via stored energy, known as surface energy. Changes in this surface energy, for example due to atomic reorganization from elastic work, causes modifications in surface stress and vice versa.68 Adsorbates have been known to cause drastic reconstructions in surfaces by breaking and making new bonds in the surface material. However, until the late 1970s it was assumed that in the absence of such reconstructions, surface structure was not affected. However, after this point it was observed that even in the lack of extreme reconstruction, average surface interlayer spacings were affected69 – surface atoms often are displaced along the surface, move outwards, or rotate.3 These induced atomic displacements typically amount to a position change of 0.05-0.10Å. Nearly every adsorbate interaction examined on low-index metal surfaces exhibits these lateral relaxations and/or buckling.70-77 For example, sulfur, oxygen, and carbon all induced compressive surface stresses upon adsorption to a Ni(100) surface (Figure 1-3). Phonon dispersion measurements estimated that the distance of surface atoms were expanded by ~5% and that the adsorbate induced compressive stress exceeded the tensile stress of the clean surface by three times.64 It has also been observed that the adsorption of electron donating moieties, such as Cs or Ni atoms,
exacerbate inherent surface tensile stress. It should be noted that the viewpoint of Cs and Ni as simply electron donating moieties is overly simplified. In fact, the nature of the interaction between alkali metals and surfaces was at one point highly contested in the literature. After many studies it was determined that rather than a straightforward donation of electron density, the interaction of an alkali metal with a surface generated more of an “electron cloud” at the surface.\textsuperscript{78-88} By modification of the surface energy through atomic reorganization, the extent of surface relaxation/reconstruction has been shown to be directly related to the strength of interaction between the adsorbed species and the surface.\textsuperscript{89,90}

Figure 1-3. Induced surface stress of as a result of oxygen, sulfur, and carbon adsorption on Ni(100). Reproduced with permission from ref 64.
After the realization that atomic reorganization at surfaces was related to surface stress, more effort was put towards understanding the nature of various adsorbate interactions. For example, in 1997 Beardmore et al conducted first principles calculations that revealed that the ubiquitous gold-thiol bond resulted in gold atoms losing electron density to sulfur atoms, a 0.2e⁻ charge transfer. This effectively reduces the Au-Au bond strength at the surface, increases Au-Au interatomic distance, and decreases the density of Au surface atoms. The direct consequence of this is \( \approx 6 \text{ N m}^{-1} \) of compressive surface stress that can modify the natural reconstruction of the gold surface, ejecting Au surface atoms that diffuse to form etch pits, or vacancy islands. It has also been theorized that the change in surface stress could arise from many interaction mechanisms of adsorbates, including the electrostatic effects, van der Waals forces, dipole-dipole interactions, changes in hydrogen bonding, etc. This was studied by Grossmann et al, who observed that thin heteroepitaxial films could bear a large amount of surface stress, far beyond what was expected to be present from lattice misfits. It was proposed in this instance that large stress values were a result of charge transfer between the adlayer and the substrate, not intra-adlayer interactions.

The backbonding model of adsorption, introduced by H. Ibach in 1994, can predict the behavior of many adsorbate interactions, especially those in cases that involve strong heteropolar bonding. However, one example of where the backbonding model breaks down is in the case of H adsorption on Pt(111), a case that only involves a small charge transfer. A 1997 P. Feibelman work calculated that the
induced surface stress from H adsorption is compressive despite the fact that based on the work function change, hydrogen appears to be an electron donor.\textsuperscript{108} Feibelman additionally pointed out a discrepancy in the backbonding model, where in some instances, the empty orbitals presented by surface atoms are antibonding, such as in the case of Pt and Ni. Charge donation from adsorbates into these surfaces would result in a filling of these antibonding orbitals and therefore an increase in the equilibrium bond distance, causing a compressive stress. However, this is in contrast with the majority of experimental observations.\textsuperscript{78, 108} The other issue with the backbonding model that Feibelman described is in the scanty evidence for the correlation between surface relaxation and the magnitude/sign of surface stress in a metal, using the Pt(111) surface as a prime example. Despite having a tensile surface stress, the surface layer of Pt(111) atoms is slightly expanded rather than contracted. There are other examples of metal surfaces in the literature that relax outwards as well, namely Pd(001) and Rh(001).\textsuperscript{109}

Another work following Ibach’s also examined their results in terms of his backbonding model.\textsuperscript{64, 109} Nichols et al used the well understood surface electrochemistry of Au(111) in acid to better understand how accurate the backbonding model is in describing adsorbate behavior. The electrochemical environment allowed for measurements to be made on an unreconstructed surface. It is expected from Ibach’s model that a relieving of the natural tensile surface stress would lead to a lattice expansion. However, it was experimentally observed that the Au(111) surface in electrolyte solution actually exhibited a compressive change when
positively charged. It was pointed out that where the backbonding model breaks down is in failing to account for energetic contributions to the electronic structure of the surface. This and other studies have determined that surface relaxation is a tradeoff between two effects: the cohesive force between adjacent atoms and the band energy due to the band structure of the metal.\textsuperscript{109, 110} A way to determine the balance of these two variables for a given system is to calculate the density of states (DOS) of a relaxed and unrelaxed surface (Figure 1-4). The DOS for an Au atom sees its major contribution from $d$ orbitals and a smaller contribution from $s$ orbitals. The difference between the relaxed and unrelaxed DOS was observed to be positive for low energies and negative closer Fermi edge, suggesting that the relaxed surface is depleted of DOS near the Fermi edge and enriched between -4 to -1 eV. This would result in an increase in energy and outward movement of Au surface atoms from their unrelaxed positions. A simulated removal of states at the Fermi level (by Cl adsorption) demonstrated a relaxation inward of $\sim$1\%. These data improved upon the understanding of adsorbate-induced atomic relaxations by introducing the band structure of the surface as a competing force against atomic cohesion. When DOS are removed from the surface, outward relaxation is hindered, and inward relaxation is promoted. This is in stark contrast to the way positive surface charging adds to the DOS and stimulates outward relaxation in the electrochemical Au(111) system.\textsuperscript{109}
Figure 1-4. The DOS of an Au atom for surfaces representing relaxed, unrelaxed, and a Cl-covered surface. Reproduced with permission from ref 109.
Despite the understanding from the surface science literature that molecular adsorption results in atomic distortion and surface stress modifications, there is no prediction or modelling from this community to show how this might impact systems on the macroscale. Additionally, though the backbonding model accurately describes many adsorbate-metal surface systems, it is not a nuanced enough depiction to capture all the factors at play. This is clear from studies that find an importance in based on the band structure and DOS of the metal, suggesting that in order to build a complete, bottom-up picture of metal-adsorbate interactions, one must have a thorough understanding of the band and orbital configurations that impact bonding. Therefore, the next discussion will focus on how to interpret and predict bonding between an organic molecule and a metal surface in terms of molecular orbital (MO) theory and band theory.

1.6. Adsorbate-Metal Interactions in the Context of Molecular Orbital and Band Theory

The minimization of surface energy is the major driving force behind the vast majority of surface processes and phenomena, like those discussed in this review. The free energy of metal surfaces rises and falls with cohesive energy, resulting in large surface energies for transition metals whose \(d\)-orbitals are partially filled. This is why such metal surfaces are generally covered with organic molecules (hydrocarbons, oxides, water, etc…) under ambient conditions, as a way to decrease surface energy.
These interactions between organic adsorbates and metal surfaces can be understood in terms of molecular orbital (MO) theory, which is what we will discuss here.\textsuperscript{111}

For a simple heteroatomic molecule, A-B, the linear combination of atomic orbitals upon bonding between A and B results in two molecular orbitals. One MO is lower in energy, the bonding orbital, and one orbital is higher in energy, the antibonding orbital – the difference in energy between the two is a function of the atomic orbital overlap (Figure 1-5). Each of the two molecular orbitals can contain an

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{molecular_orbital.png}
  \caption{Molecular orbital generation from the linear combination of atomic orbitals, and the subsequent evaluation of binding strength upon the filling of molecular orbitals. Reproduced with permission from ref 111.}
\end{figure}
electron pair, and the filling of these orbitals determines the A-B bond strength. The strongest bonding between A and B occurs when the bonding MO is filled, and a repulsive interaction between A and B occurs when both the bonding and antibonding MOs are filled. In an intermediate case, fully filled bonding and partially filled antibonding orbitals result in a weak interaction.

The DOS corresponds to the number of states that can be occupied by electrons at each energy level in a metal. There is broad band of delocalized electrons, corresponding to the s and p orbitals (low DOS), and a narrower band of localized d electrons (high DOS) (Figure 1-6). Metallic bonds can be understood as a collection of MOs shared between the numerous atoms of a metallic solid, being close enough to form a continuous “band”. These bands behave like the orbitals of a molecule; if there is poor overlap between electrons, the interaction is weak, resulting in a narrower band, as in the case for the d electrons of a metal. However, the wavefunctions for the s and p electrons overlap greatly, resulting in them being the delocalized “sea of electrons” typically associated with metals. The band associated with these electrons is much broader. Due to this parallel in MO and band theory, the comparison can be extended; the lower levels of the band structure are bonding, the higher levels antibonding, split by the Fermi level of the metal.
Group VII transition metals have a partially filled d band, resulting in the Fermi level bisecting the d band, whereas group IB metals have a filled d band. In this instance, the Fermi level falls above the d band and intersects the diffuse s band. Upon interaction between an adsorbate molecule and the surface of a transition metal, the molecular orbitals of the adsorbate overlap with the band structure of the metal, creating new pseudo-molecular orbitals (Figure 1-7). The filling of these new states determines the strength of the adsorbate-surface interaction.
Figure 1.7. A molecular orbital theory framework for evaluating the strength of interaction between a molecule and a d metal surface. Reproduced with permission from ref 111.

This summary of MO and band theory as it relates to adsorbate bonding is, of course, an extremely simplified version of a realistic adsorbate-surface interaction. However, it provides a basic understanding for how to think about chemisorption and the intrinsic stresses that may be produced. A weaker interaction will produce less surface stress, and a stronger interaction more. For a system-specific evaluation of how the molecular orbitals of an adsorbate interact with the band structure of a metal surface, DFT simulations must be performed.\textsuperscript{109,112} At this point, the understanding of adsorbate induced stresses in metal surfaces and its effects on global behavior is still in its nascent stages, despite many decades of research from both ends of the size spectrum. One way to connect these two areas is to study these same effects in an
intermediate length scale – the nanoscale. Nanoscale structures have unique global behaviors different from bulk-scale materials that are in-part due to surface effects. Recent advances in instrumentation\textsuperscript{113} allow for the observation of not only atomic structural details of nanoparticles, but also their general behavior. This presents a unique opportunity to bridge the continuum-based with atomic-scale observations. The final section of this review will briefly discuss the impacts of molecular adsorption on the structural and performance of nanoparticles.

1.7. Looking Forward: Ligand Mediated Phenomena in Nanoparticles/Nanoclusters

It has already been pointed out by previous researchers, that metal nanoclusters can be seen as a species comprised of all surface atoms, due to the fact that there are no actual “bulk-like” atoms in them.\textsuperscript{3} Structural and vibrational comparisons of bonding at metal surfaces and in complexes containing few atoms validates this view, suggesting that the local structure and properties of adsorbates on surfaces and metal clusters is amazingly alike.\textsuperscript{114} In 2000, first principles calculations demonstrated that the binding of thiol molecules to gold nanoclusters not only leads to a redistribution of charge density, but also cause surface lattice expansion of \textasciitilde 20\% amongst gold atoms closest to sulfur binding groups. Both of these observations were consistent with the behavior of gold surfaces upon adsorption of thiols.\textsuperscript{115} Later studies on small gold nanocrystals also observed that thiol binding produced highly disrupted Au-Au
bonds, \textsuperscript{116} large (300 nm) nanocrystals presented thiol-induced deformations penetrating relatively far into the surface (20 nm), towards the nanocrystal core.\textsuperscript{117} Though the case of thiol ligands on gold nanoclusters and particles represents a strong, near-covalent interaction, a similar trend holds true for weaker interactions. For instance, recent studies found that lattice spacing in Pt nanoclusters capped with PVP ligands ranged from 0.95-2.56\% greater than bulk values.\textsuperscript{118,119}

However, ligands (footnote) have also been observed to facilitate drastic global crystallographic restructuring in nanomaterials. For instance, it was experimentally observed that phosphine-stabilized gold clusters smaller than Au39 have a core with a cuboctahedral structure, whereas larger clusters undergo a core transition from cuboctahedral to a close-packed, more bulk-like, structure.\textsuperscript{120-122} In another study, extremely thin gold square nanosheets (AuSS) synthesized in oleylamine had a native hcp crystallographic structure.\textsuperscript{123} Upon complete exchange of oleylamine for octadecanethiol ligands, it was observed that the crystallography of the AuSSs transformed to a fcc structure. When a low concentration of octadecanethiol was added, there was insufficient exchange with oleylamine. The resulting structures were irregularly shaped Au nanosheets with poor crystallinity. The complete transformation from hcp to fcc was found to be independent of alkane chain length, hydrophilicity, and functional groups, suggesting that the thiol binding chemistry was the main factor in facilitating the crystallographic transformation.\textsuperscript{123}

Beyond structural effects, there is a growing appreciate for the effects of ligands on other nanoscale properties, such as photoluminescence. In the case of
quantum dots, it has been observed that ligands of different length alkane chains will modulate the photoluminescence lifetime due to differential surface passivation and the elimination of surface trap states. For small gold nanoclusters, strongly binding ligands increase the quantum yield of the photoluminescence by reducing vibrational, non-radiative relaxation pathways. In chapter 3 of this thesis work, we introduce a new nanoscale effect where we demonstrate that the binding strength of nanoparticle ligands changes the overall mechanical behavior of the system, representing a transition towards understanding the effects of molecular adsorption on surfaces from a multi-scale perspective.

1.8. Conclusion

While much work has been done towards understanding the interaction of molecular adsorption to surfaces and its effects, the fields that study this remain relatively isolated from one another. Cantilever based systems observe deflection upon molecular adsorption, a phenomenon that can be understood in terms of adsorbate-induced surface stress. However, measures taken to form a mechanistic understanding of these interactions often result in many literature reports that contradict one other. This is a function of the fact that cantilever systems are highly uncontrolled due to their preparation - evaporation of gold leads to surfaces with different crystallinities, and therefore, different behavior upon adsorbate binding. A continuum-based approach to this system does not acknowledge the variation in evaporated surfaces, resulting in seemingly contradictory results in different
experimental setups between research groups. Additionally, surface stress is a continuum level construct that undoubtedly arises from atomic factors, but the cantilever literature has not explored these. On the other hand, surface science has produced a great deal of detailed work that demonstrates how atoms at surfaces reorganize upon interaction with adsorbates but does not explore the macroscale implications of this. Additionally, even though the backbonding model in surface science can predict the behavior of many surface interactions, it does not include the important contribution of the DOS of the metal surface. This results in instances where the backbonding model does not provide the correct predictions of adsorbate-surface behavior. One way to understand these interactions more accurately is under the framework of MO theory, where the strength of a molecular interaction with a metal surface relies on the overlap and filling of MOs. Nanoscale systems provide a unique experimental opportunity to examine both the macroscale behavior as well as the atomic effects of organic molecular interactions with metal surfaces. By combining these fields in the context of nanoscience, one can not only build a multiscale understanding of adsorbate-surface interactions, but also explore new nanoscale effects.

1.9. Thesis Overview

Chapter 2 describes the synthesis and characterization of a highly compliant, thin metal nanoplate when deformed over a templated substrate. We determined that VdW interaction energy between the substrate and the nanoplate was high enough to
cause plastic deformation, as verified by analytical modelling and simulations. Additionally, we characterize the presence of unique bend contours that appear in TEM experiments and determine that they are directly related to the lateral extent of deformation in the nanoplate. Finally, it was demonstrated that based on the morphology of the templated substrate, several more complicated curvilinear geometries could be built. This work was published in 2021 in *Nano Letters*.113

Chapter 3 uses the experimental system established in Chapter 2 as a means for investigating the effects of ligand chemistry on a thin, highly compliant nanoplate. When functionalized with a library of ligands of increasing binding strength, we observed that the mechanical strength of the nanoplates increased. Continuum-scale modelling demonstrates that the nanoplate can be modelled as a core-shell structure, where the shell corresponds to the first few metal atom layers. Our experimental results are corroborated using this model by increasing the yield strength of the nanoplate shell. We also compare how ligand chemistry affects the interatomic spacing of the nanoplates, and how this compares to other experimental results in order to build a multiscale understanding of nanoparticle-ligand interactions. This work will be featured in a subsequent, peer-reviewed publication.

Chapter 4 is a perspective that reviews the technique of liquid-phase TEM, an extremely powerful tool for characterizing nanostructures. We describe advances in technology that resulted in the realization of the technique as well as current challenges with it, namely the radiolysis of liquid by the electron beam. We suggest that perhaps radiolytic products can be used as a tool for sample perturbation rather
than a source of error, and present design rules to potentially tailor the production and distribution of radiolytic species. The understanding and innovation where characterization tools are concerned is of the utmost importance for the continued advancement of knowledge in the field of nanoscale materials. This perspective was published in 2018 in *ACS Energy Letters*.¹¹³

Chapter 5 provides general conclusions from the work presented and an outlook of the future directions of using the systems described as a method for building new, dynamic nanostructures as well as providing an unprecedented look at the consequences of surface interactions.

The Appendix presents work completed that is topically unrelated to that presented in the main body of the thesis. It describes the formation and characterization of (semi)hollow nanoparticles based on an Ag-Au galvanic replacement in non-aqueous solvents. This work was published in 2018 in *Particle and Particle Systems Characterization*.¹¹³
Mechanical Reshaping of Inorganic Nanostructures with Weak Nanoscale Forces

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2 Reprinted, with permission from: Sarah M. Rehn; Theodor M. Gerrard-Anderson; Liang Qiao; Qing Zhu; Geoff Wehmeyer; Matthew R. Jones, Mechanical Reshaping of Inorganic Nanostructures with Weak Nanoscale Forces. *Nano Lett.*, **2021**, 21, 130-135.
2.1. Abstract

Inorganic nanomaterials are often depicted as rigid structures whose shape is permanent. However, forces that are ordinarily considered weak can exert sufficient stress at the nanoscale to drive mechanical deformation. Here, we leverage van der Waals (VdW) interactions to mechanically reshape inorganic nanostructures from planar to curvilinear. Modified plate deformation theory shows that high aspect ratio 2D particles can be plastically deformed via VdW forces. Informed by this finding, silver nanoplates were deformed over spherical iron oxide template particles, resulting in distinctive bend contour patterns in bright field (BF) transmission electron microscopy (TEM) images. High resolution (HR) TEM images of deformed areas reveal the presence of highly strained bonds in the material. Finally, we show the distance between two nearby template particles allows for the engineering of several distinct curvilinear morphologies. This work challenges the traditional view of nanoparticles as static objects and introduces methods for post-synthetic mechanical shape control.

2.2. Introduction

Nanoscience is predicated on the idea that properties are dictated by nanoscale structure in the form of particle size and shape. In the case of inorganic systems, structure control is most often exerted either during the synthesis to generate a desired particle morphology, or post-synthesis to site-specifically
remove/deposit material or assemble building blocks into superstructures.\textsuperscript{128-134}

Absent among these strategies is the possibility to physically re-shape or re-form inorganic particles via mechanical forces rather than chemical manipulation.\textsuperscript{135-137} Previous reports have investigated the mechanical properties of nanomaterials through nanoindentation and other \textit{in situ} methods.\textsuperscript{138-145} However, these approaches are low-throughput, single-particle techniques that are often focused more on measuring mechanical properties rather than exercising structural control. Flexibility has been observed in certain nanostructures, but this is often a consequence of random sample preparation processes.\textsuperscript{146-148} The mechanisms driving deformation, their size dependence, and the ability to create new morphologies via flexibility remain unclear.

Here, we show that ubiquitous van der Waals (VdW) interactions, which are often considered weak compared to most nanoscale forces, can be leveraged to mechanically deform inorganic nanostructures as a means of post-synthetic shape control. To explore the feasibility of this method, a mathematical model was developed based on continuum mechanics theories for plate deformation. Using the conclusions from this analysis, we show the ability to control the shape of high aspect ratio silver nanoplates by deforming them over small iron oxide template nanospheres. The local deformation caused by a single template particle can furthermore be used as a structural motif to create several unique curvilinear structures. This work challenges the conventional notion that nanoparticles are rigid objects and introduces a new class of curvilinear nanostructures.
2.3. Results and Discussion

To understand the forces that might result in nanoparticle deformation, we assumed that typically weak VdW interactions could be leveraged in a situation in which plate-shaped particles interacted with a surface, since this geometry maximizes the VdW contact area compared to other particle shapes. Additionally, we chose to work with noble metal nanoparticles as they are known to be particularly ductile and can readily be synthesized into 2D morphologies.146, 149-151 To probe the response to a mechanical stressor under these conditions, Kirchhoff-Love plate theory was employed, which models the elastic deformation and stress behavior of two-dimensional structures. In this formalism, an equilibrium state of mechanical stress is described by a fourth-order partial differential equation, to which there are few tractable solutions. One of the simpler analytical solutions assumes the axially symmetric deformation of a circular disc under a point load (Figure 2-1a, inset). Modifying this solution to account for plastic deformation allowed us to compare the relative strength of VdW interactions and mechanical strain energy experienced by nanoplates (see Supporting Information). Given some reasonable assumptions, this analysis demonstrates that plates with a thickness of <10 nm and an
Figure 2-1. Deformation of thin, silver nanoplates over spherical template particles. (a) Thickness-dependence of the VdW and strain energies as calculated by modified Kirchhoff-Love plate theory. Inset shows the geometry of the strain energy calculation, where $F$ is the concentrated force and $a$ is the disc radius. Schematics of the (b) top-down and (c) cross sectional view for a nanoplate deformed over a spherical template particle. (d) Representative
TEM image of a silver nanoplate deformed over one template nanoparticle, (e) a closer look at the unique bend contour that is observed and f-i) several examples of the bend contours that were seen in every instance of a deformed structure.

aspect ratio of ~100 represent a transition point, below which VdW interactions are capable of causing a significant particle shape transformation (Figure 2-1a, see Supporting Information). Importantly, these findings hold for several other common inorganic nanomaterial systems (e.g., SiO₂, CdSe) and thus indicate the generalizability of VdW-driven mechanical reshaping (Figure S2-12 and 13).

Importantly, the mathematical solution describing plate deformation used above can be translated to and investigated in an experimental context. High aspect ratio silver nanoplates of ~8 nm in thickness were synthesized and deformed over spherical iron oxide template particles to mimic a concentrated, axially-symmetric load (Figure 2-1a inset, b and c). The resulting regions of mechanical strain are evidenced by six-lobed deformation patterns in Bright Field (BF) TEM data (Figure 2-1d and e). The unusual pattern of contrast, known as a bend contour, was seen in every instance in which a nanoplate was conformally draped over a spherical template (Figure 2-1f to i). Bend contours are a phenomenon that occur when local strain causes nearby crystallographic planes to change their orientation and diffraction condition, resulting in variations in contrast. Although bend contours are well-known features of thin TEM samples, they most often extend over
Figure 2-2. Selected area electron diffraction and dark field analysis of bend contours. (a) BF TEM image of the bend contour used for further analysis. (b) Indexed SAED of the deformed nanoplate revealing the expected 1/3(422) diffraction spots arising from twinning along with first order (220) diffraction spots, and (c-h) DF TEM images corresponding to these spots. (i) 3D AFM topographical map of a nanoplate with axially-symmetric deformed areas.

Large distances and represent gradual changes in the orientation of the material’s lattice. The highly symmetric and punctate nature of the bend contours observed in our samples is unusual and points to a localized stress gradient surrounding the spherical particle template. The diameter of these bend contours extended about an order of magnitude larger than the size of the template itself (103 ± 11 nm, n=228), validating the assumption of a point load in the plate theory model (Figure 2-1a).

To confirm whether the 6-fold symmetry of the observed bend contours is related only to an electron diffraction effect and not a real-space morphological feature, we performed selected area electron diffraction (SAED) and dark-field (DF) TEM analysis. The SAED of a deformed nanoplate exhibits a set of six spots closest to the transmitted beam that represent the 1/3(422) forbidden reflection which is a known feature of structures with internal twinning (Figure 2-2a,b).\textsuperscript{155} The brighter set of six spots represents the first order diffraction from (220) planes that reveal distinct deformation lobe pairs when selected for in DF TEM imaging (Figure 2-2c-h). Therefore, the bend contours that appear in BF TEM images are the convolution of symmetric deformation lobes occurring via (220) planes because the nanoplate is oriented along the [\textit{1\textit{1\textit{1}}}] zone axis (Figure 2-2c-h). Atomic force microscopy (AFM)
topographical maps show smooth, axially-symmetric features around template-based deformed regions and are in agreement with bend contour sizes measured by TEM (Figure 2-2i, S2-3). This confirms that the geometry of the proposed model based on plate theory is appropriate for understanding nanoscale shape control.

To further validate these findings, experimental and theoretical results were compared against elastic finite element simulations (COMSOL Multiphysics) using a

Figure 2-3. Comparison of experimental and theoretical displacement fields with FEM simulation results. (a) Topographical data from several AFM scans are shown in black. Deflection fields generated from a clamped disc model in both Kirchhoff-Love plate theory (red) and COMSOL (blue) are in good agreement, validating the analytical modeling. Deflection of a triangular nanoplate model in COMSOL (green) do not describe the experiments,
showing that plate-substrate clamping due to VdW forces is essential. (b) COMSOL-generated 3D map of von Mises stress (color scale) for a Ag nanoplate with elevated Young’s modulus value of 125 GPa. Template-based deformation results in stresses in excess of yield over most of the plate volume.

geometry identical to the Kirchhoff-Love model (Figure 2-3). The theory and the simulations utilize some of the same input parameters (e.g., boundary conditions, mechanical constants), but employ different loading conditions and solution methods (see Supporting Information). Experimental height profiles of several deformed nanoplates gathered via AFM measurements (black dots, Figure 2-3a), show excellent agreement with the displacement fields generated from both the analytical theory and the finite element simulations (Figure 2-3a). While the Kirchhoff-Love theory utilizes a point load to achieve deformation, the simulations explicitly employ the experimental geometry of a small sphere deforming a nanoplate. The agreement between the experimental, simulation-based, and theoretical deflection fields, particularly surrounding the center of the deformed region (x = 0, Figure 2-3a), suggests that the approximation of a point load in the theory is reasonable. Quantification of the contact radius between the template particle and nanoplate was determined from simulations to be ~5 nm, an order of magnitude less than the radius of the deformed area itself (see Supporting Information); this finding further supports the assumption of a point load. Importantly, if instead of considering only the axially-symmetric deformed region, simulations are performed with the entire triangular plate geometry, displacement fields are found to extend over considerably
larger length scales (i.e., 200-300 nm) and no longer agree with experiment (green line, Figures 2-3a, S2-18 to 21). Since sedimentary forces are negligibly small for particles of nanometer dimensions, this result suggests that only attractive VdW forces can explain the local deformation observed in these structures.

The simulation results also allow us to generate three-dimensional plots of the internal stresses experienced for plates with a given displacement (Figure 2-3b). This information can be used to further understand the structural consequences of VdW-driven nanoparticle shape control by mapping regions for which the yield condition has been surpassed and permanent (plastic) deformation has occurred. Although the bulk yield stress of Ag (54 MPa) is surpassed across the entire volume of the plate, it is well known that metal nanostructures often have higher Young’s modulus and yield stress values than their bulk counterparts.\textsuperscript{156-161} Quantitative measurements of nanoparticle mechanical constants vary considerably and likely depend sensitively on crystal orientation, dimension, and internal defect structure. Nonetheless, we performed multiple simulations using both bulk and elevated Young’s modulus values, appropriate for silver.\textsuperscript{156-161} In all cases, the resulting stresses well exceed even the elevated yield stress values (~1 GPa) expected for nanometer-scale silver particles (Figure 2-3b, see Supporting Information). This numerical result suggests that plastic deformation is widespread across the volume of the silver nanoplates displaced by template spheres. This conclusion is corroborated by the fact that if plastic deformation is ignored in the Kirchhoff-Love theory, the energy required to achieve the observed displacement far exceeds what is available to the system in the
form of VdW or other attractive interactions. Only by modifying the theory to account for the possibility of plastic deformation do we observe agreement between theory and experiment (see Supporting Information).

Figure 2-4. Experimental evidence of severe lattice distortion and strain from plastic deformation. (a) High resolution TEM image of a deformed region and (b) corresponding FFT. The position of bright spots indicate the spacing of (220) lattice planes. Differently colored rings in the FFT correspond to varying atomic spacing. (c) High resolution TEM image showing both normally spaced atomic planes (red) and severe lattice distortions (orange) resulting from deformation.

The curvilinear morphology created by the deformation of nanoplates tilts crystallographic planes and strains the crystal lattice, causing atomic-level distortions. To further understand the role of bond strain and plastic deformation in silver nanoplates, we performed high resolution TEM imaging of regions surrounding the spherical template nanoparticles (Figure 2-4). Fast-Fourier Transform (FFT) of these images showed a set of six spots that appear more diffuse in the radial direction compared to analogous spots in the experimental SAED pattern (Figure 2-4b). This
reflects the presence of distortion in the atomic Ag lattice, spanning a range of different values. To quantify this, three different rings (red, yellow, cyan) were placed at different radial positions over the diffuse spots in the FFT to denote different degrees of lattice distortion, expressed as a percentage deviation from the unstrained lattice spacing (Figure 2-4b and inset). This measurement reveals a deviation of 0-5% or more over the vast majority of the deformed region being imaged. This indicates a degree of lattice distortion significantly above what is ordinarily considered the limit of elastic bond strain, further confirming the necessity of including plastic deformation in the model for nanoplate mechanics.\textsuperscript{162-164} Additionally, atomically resolved images show lattice planes and atom positions that are severely distorted with respect to a perfect crystal, indicating numerous broken bonds, defects, and plastic mechanical behavior (Figure 2-4c). It is important to note that there exist regions of elastically strained metal bonds throughout the structure that are consistent with what has been observed to transform a normally inactive noble metal surface to one that can catalyze chemical reactions.\textsuperscript{165-167} This suggests that such curvilinear nanostructures might have a high density of active sites for heterogeneous catalysis.
Figure 2-5. Engineering of coupled curvilinear structures. (a) A single bend contour is observed when two template particles are in physical contact or are extremely close to one another. As two template particles move a distance, $d$, apart from one another, (b) a single distorted bend contour with a bridged region is observed that eventually becomes (c) two distinct contours with a saddle point between them. (d) Eventually, the two templates are far enough apart that isolated bend contours are present with complete structural relaxation between them. A colormap was applied to BF TEM images to enhance differences in contrast for the purpose of analysis (Figure S2-5).

In traditional nanoscale systems, there are canonical structures from which more complex architectures can be built (e.g., spheres assembled into a superlattice or rods lithographically fabricated into metamaterial arrays). Similarly, we imagined the morphology associated with a single template particle might serve as a basic structural motif for building more complex curvilinear structures. In order to achieve this, we have investigated the topographies that result when two template particles are near one another and deformed regions overlap (Figure 2-5). If the
parameter \( d \) is defined as the spacing between nearby template spheres, \( d = 16-31 \) nm generates a single bend contour that appears slightly larger than one associated with a single template particle (Figure 2-5a). Two templates that are separate but closely spaced (\( d = 37-65 \) nm) show a distorted six-lobed pattern with a region bridging the two particles (Figure 2-5b). Interestingly, when \( d \) increases to \( \sim 70-93 \) nm, a saddle point is observed, consisting of areas of high lattice compression between particles and lattice tension over the template peaks (Figure 2-5c). Lastly, templates that are greater than \( \sim 94 \) nm apart display bend contours that are completely decoupled from one another (Figure 2-5d). This method relies on the mutual mechanical relaxation of neighboring deformation fields and opens up the possibility for complex curvilinear architectures based on substrate topography rather than lithographic patterning.

2.4. Conclusion

In this work we report a simple method for post-synthetic nanoparticle shape modification via mechanical deformation rather than chemical manipulation. Calculations using Kirchhoff-Love plate theory modified to account for plastic deformation create a framework from which to understand the interplay of forces that facilitate this new type of morphological control. Using this in conjunction with simulations and experimental findings, we demonstrate that weak VdW forces can indeed generate enough energy to drive mechanical strain and thereby create a new class of curvilinear structures based on substrate topography. Since these objects
would be difficult to generate lithographically, they are expected to result in previously inaccessible electromagnetic modes relevant to the nanooptics community.\textsuperscript{169,170} Furthermore, the gradient of strained bonds in these materials has implications for their performance or study in catalytic systems.\textsuperscript{165-167,171} Overall, this work demonstrates that inorganic nanoparticles may be thought of as being capable of dynamic structural changes, actuated by simple and ubiquitous nanoscale forces.

\subsection*{2.5. Funding Acknowledgement}

M. R. J. would like to acknowledge financial support from the Robert A. Welch Foundation (Grant C-1954) and the David and Lucile Packard Foundation (Grant 2018-68049). G.W. and Q.Z. would like to acknowledge funding support from the Robert A. Welch Foundation (Grant C-2023). S.M. R. would like to acknowledge financial support from a National Science Foundation Graduate Research Fellowship #1450681. The authors would like to acknowledge financial support from Rice University.

\subsection*{2.6. Experimental Methods and Supporting Information}

\subsubsection*{2.6.1. Chemicals and Materials}

All chemicals were used as purchased with no further purification or processing. Trisodium citrate (Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7} • 2H\textsubscript{2}O, 99.0\% ACS Reagent), silver nitrate (AgNO\textsubscript{3}, 99.9999\% trace metals basis), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 30\% w/w
in water ACS reagent with inhibitor), sodium borohydride (NaBH4, 99.99% trace metals basis), and L-ascorbic acid (C6H8O6, 99.0% bioXtra) were purchased from Sigma Aldrich. Acetonitrile (C2H3N, ChromAR) was purchased from Macron. The PEG-thiol molecule used for nanoprism stabilization, HS-C11-(PEG)6-COOH, was purchased from Prochimia Surfaces. Oleic acid capped iron oxide nanospheres (15 nm) in chloroform were purchased from Ocean NanoTech.

2.6.2. Preparation of Ag Nanoplate Seeds

Ag nanoprism seeds were prepared following a previously published protocol. Seeds were prepared in an aqua regia-cleaned scintillation vial by combining fresh nanopure water (20 mL), trisodium citrate (1.2 mL, 75 mM), AgNO3 (0.020 mL, 100 mM), and H2O2 (0.048 mL, 30% w/w) under vigorous stirring. To this, a freshly prepared solution of NaBH4 (0.120 mL, 100mM) was injected, and the reaction progressed over a 30-minute time period where the solution initially turned yellow and progressed through several color stages that finally ended at a cerulean blue. The nanoprism seeds were stored on a benchtop at room temperature.

2.6.3. Seeded Growth of High Aspect Ratio Silver Nanoplates

The growth of high aspect ratio silver nanoparticles was adapted from a previously published report. To an aqua-regia cleaned scintillation vial in an ice bath, fresh nanopure water (10 mL), acetonitrile (5 mL), trisodium citrate (0.200 mL, 75 mM), and ascorbic acid (0.100 mL, 100 mM) were added under vigorous stirring.
Meanwhile, an aliquot of the previously prepared seeds was subjected to centrifugation (10 minutes, 20133 rcf) to remove unreacted precursors. After the spin cycle, the supernatant was removed and the pelleted nanoprisms were concentrated 5x via resuspension in fresh nanopure water. These concentrated silver nanoprisms seeds were immediately added to the reaction vial (0.035 mL), after which AgNO3 (0.120 mL, 100 mM) was injected. This slow growth reaction proceeded to stir vigorously in the ice bath for approximately two hours, yielding a very pale blue solution, before being moved to the refrigerator to finish growth overnight, after which that large silver nanoprisms had visibly settled out of solution as a grey precipitate. Upon disturbing the precipitate, the solution appeared to be blue with a grey pearlescent quality, indicating the presence of the large, light scattering nanoprisms. Grown nanoprisms were then stabilized before further characterization by incubating an aliquot of the as-synthesized nanoprisms with a PEG-thiol molecule (0.100 mM) at 4°C under shaking overnight.

### 2.6.4. Preparation of TEM and AFM Samples

Iron oxide nanospheres (0.001 mL) were freshly diluted into toluene (15 mL). Large silver nanoprisms were spun down (1 min) with a tabletop centrifuge, supernatant was removed, and the nanoparticle pellet was resuspended with an equal volume of fresh nanopure water. To prepare a TEM sample, diluted iron nanoparticles (0.0035 mL) were drop cast onto a TEM grid. After the grid dried, washed nanoprisms (0.0065 mL) were drop cast onto the same grid and dried under
vacuum. All wide field BF, DF, and SAED data were obtained with a JEOL 1230 High Contrast TEM operated at 80 kV. High resolution TEM data were obtained with a JEOL 2100 FEG TEM operated at 200 kV. All size analysis from TEM images was done using ImageJ. To prepare AFM samples, diluted iron nanoparticles (0.015 mL) were drop cast onto a mica disc and dried under vacuum. After drying, washed nanoprisms (0.030 mL) were drop cast onto the same disc and dried under vacuum. All AFM data were obtained with a Park NX20 AFM using tapping mode.

2.6.5. Experimental Supporting Figures

![Representative BF TEM images of (a) silver nanoprisms seeds and (b) a grown, high aspect ratio silver nanoprisms.](image)

**Figure S2-1.** Representative BF TEM images of a) silver nanoprisms seeds and b) a grown, high aspect ratio silver nanoprism.
Figure S2-2. Representative BF TEM images of iron oxide nanospheres obtained from Ocean NanoTech. Size analysis of TEM images with ImageJ revealed the size distribution to be $15 \pm 1$ nm ($n = 159$). Iron oxide nanoparticles were used as templates due to their high degree of shape and size uniformity.

Figure S2-3. Collective AFM data of many deformed nanoprism structures ($n = 20$), fitted with to a Gaussian. The FWHM of these data is 66 nm, which matches well with the bend contour diameter data from TEM analysis.
Nanoprism thickness was also measured with AFM and found to be 8.8 ± 1.3 nm (n = 24). These data can be found normalized in the main text Figure 2-3a.

Figure S2-4. Wide field TEM image of the particle used for dark field analysis in main text Figure 2-2.
Figure S2-5. Example TEM image to demonstrate the colormap applied to images in main text Figure 2-5. The colormap was applied to help highlight differences in contrast that may be difficult to decipher in the grayscale image. Four-color map was directly applied to image with Adobe Photoshop.

2.6.6. Modification of Kirchhoff-Love Plate Theory for Plastic Deformation

In order to calculate the strain energy for a deforming nanoplate we used Kirchhoff-Love plate theory, which is normally only valid for elastic deformation. Therefore, we made a modification that would allow strain energy to be calculated for sections undergoing plastic deformation as well as elastic deformation. This modification was required because of the large degrees of deformations for which we wanted to be able to calculate strain energies.
Figure S2-6. Diagram of the axially symmetric circular plate with a restrained edge and concentrates force acting on its center. The solid line represents the undeformed plate and the dashed line represents the deformed plate. $P$ is the concentrated central force, $w_{\text{max}}$, is the maximum displacement of the plate, and $a$ is the radius of the plate. The coordinate axes are shown.

We began with a relatively simple solution to Kirchhoff-Love plate theory; Figure S2-6 illustrates the case of an axisymmetric plate with a concentrated force applied to its center and restrained at a circular boundary distance ($a$) from the center point. This analytical will model accurately captures the circular deformed regions observed on the silver nanoplates, as well. The circular plate geometry matches the circular symmetry of the observed deformation. The point load models the force of the spherical template particle against the bottom of the plate; note that the point load assumption is reasonable because the radius of the particle is an order of magnitude less than the radius of the total deforming area. The clamped boundary condition is valid because the circular deformed
region is continuous with the surrounding plate area, which is adhered to the substrate via VdW forces. The surrounding substrate can therefore neither translate or rotate, and therefore the transition from this region to the deformed region (the boundary) is fixed. Cylindrical polar coordinates are natural for this solution and the displacement field has the following form:

$$w = \frac{w_{\text{max}}}{a^2} \left( 2r^2 \ln \left( \frac{R}{a} \right) + a^2 - r^2 \right)$$

**Equation S2-1. Displacement field of a clamped circular plate geometry.**

Where $w$ is the displacement in the $z$ axis of the neutral plane of the plate at any point $r$. The neutral plane is defined as the plane spanning the plate midway through its thickness ($z = 0$) which experiences no stress. $w_{\text{max}}$ is the displacement of the centre of the plate at the location of the concentrated deforming force ($r = 0$), $a$ is the distance between the center of the plate and the restrained edge, and $r$ is the radial coordinate. The $\theta$ coordinate does not appear in the displacement field owing to the axial symmetry of the plate geometry (Figure S2-6).

The equation for this system of elastic strain energy per unit volume, $\frac{U_{\text{elastic}}}{V}$, is as follows:

$$\frac{U_{\text{elastic}}}{V} = \frac{1}{2} \left( \varepsilon_r \sigma_r + \varepsilon_\theta \sigma_\theta \right)$$
Equation S2-2. The elastic strain energy per unit volume for the described system.

where $\varepsilon_r$, $\varepsilon_{\theta}$, $\sigma_r$, and $\sigma_{\theta}$ are the strains and stresses in the radial and polar directions, respectively. Kirchhoff-Love plate theory assumes plane stress conditions, so $\varepsilon_z$ and $\sigma_z$ are zero and so do not make an appearance. Additionally, shear strains are zero owing to the choice of coordinate system. This equation is valid until the point where the material yields. For strains beyond the yield strain, assuming fully plastic behavior, the following equation is used:

$$
\frac{U_{\text{plastic}}}{V} = (\varepsilon_r - \varepsilon_{ry})\sigma_{ry} + (\varepsilon_{\theta} - \varepsilon_{\theta y})\sigma_{\theta y}
$$

Equation S2-3. The plastic strain energy per unit volume for the described system.

where $\varepsilon_{ry}$, $\varepsilon_{\theta y}$, $\sigma_{ry}$, and $\sigma_{\theta y}$ are the strains and stresses at yielding. The lack of a $\frac{1}{2}$ term is due to stress remaining constant for increased strains after yielding. The area under the stress-strain curve is defined by a rectangle so is merely the product of the stress and strain (Figure S2-7).
Figure S2-7. Stress-strain curve illustrating elastic-fully plastic behavior. The change in the way the area under the graph, and therefore the strain energy, is calculated for regions of elastic deformation and plastic deformation is shown.

The total strain energy per unit volume for a point that has yielded is then found by combining Equation S2-2 and Equation S2-3:

$$\frac{U_{ey+p}}{V} = (\varepsilon_r - \frac{1}{2} \varepsilon_{ry}) \sigma_{ry} + (\varepsilon_\theta - \frac{1}{2} \varepsilon_{\theta y}) \sigma_{\theta y}$$

Equation S2-4. The total strain energy per unit volume of the described system.

Where $\frac{U_{ey+p}}{V}$ is the combined elastic and plastic contributions to strain energy per unit volume at a point where yielding has already occurred. In order to find $\varepsilon_{ry}$, $\varepsilon_{\theta y}$, $\sigma_{ry}$, and $\sigma_{\theta y}$, we need to define the yield criterion for this system. The von Mises yield criterion
is the most accurate for ductile metals, such as silver, so it will be used to define yielding in this system.\textsuperscript{173}

\[
\sqrt{\sigma_r^2 + \sigma_\theta^2 - \sigma_r \sigma_\theta} = \sigma_y
\]

**Equation S2-5. The von Mises yield criterion equated to the yield stress for a material undergoing a uniaxial tensile test.**

Where \(\sigma_y\) is the yield stress for the material in a uniaxial tensile test. The left-hand term represents the equivalent von Mises stress. Once the von Mises stress is equal to \(\sigma_y\), yielding has occurred and plastic deformation begins. The relations between \(\sigma_r\) and \(\sigma_\theta\) and the displacement field in the elastic range for this system are shown below:

\[
\sigma_r = -\frac{Ez}{1 - v^2} \left( \frac{d^2w}{dr^2} + \frac{v}{r} \frac{dw}{dr} \right)
\]

**Equation S2-6. The radial component of the von Mises yield stress in terms of the displacement field variables.**

\[
\sigma_\theta = -\frac{Ez}{1 - v^2} \left( \frac{1}{r} \frac{dw}{dr} + v \frac{d^2w}{dr^2} \right)
\]

**Equation S2-7. The angular component of the von Mises yield stress in terms of the displacement field variables.**
where $E$ is the Young's modulus of the material, $z$ is the coordinate in the $z$ direction, and $\nu$ is Poisson’s ratio. Carrying out the differentiations on Equation S2-1 and substituting them into Equations S2-6 and S2-7 yields:

$$\sigma_r = -\frac{4Ez\omega_{max}}{a^2(1-\nu^2)}((\nu + 1) \ln \left(\frac{r}{a}\right) + 1)$$

Equation S2-8. Simplified radial component of the von Mises yield stress in terms of the displacement field variables.

$$\sigma_\theta = -\frac{4Ez\omega_{max}}{a^2(1-\nu^2)}((\nu + 1) \ln \left(\frac{r}{a}\right) + \nu)$$

Equation S2-9. Simplified angular component of the von Mises yield stress in terms of the displacement field variables.

Equations S2-8 and S2-9 can then be substituted into the von Mises yield criterion, Equation S2-5, and then recombined with Equations S2-8 and S2-9 separately to yield the formulae for $\sigma_{ry}$ and $\sigma_{\theta y}$:

$$\sigma_{ry} = \pm \frac{\sigma_y((\nu + 1) \ln \left(\frac{r}{a}\right) + 1)}{\sqrt{(\nu + 1)^2((\ln \left(\frac{r}{a}\right))^2 + (1 + 2\nu)(1 + \nu) \ln \left(\frac{r}{a}\right) + v(\nu - 1) + 1}}}$$

Equation S2-10. The radial component of the yield stress for a material undergoing a uniaxial tensile test, in terms of the displacement field variables.
\[ \sigma_{\theta y} = \pm \frac{\sigma_y((v + 1) \ln \left( \frac{r}{a} \right) + v)}{\sqrt{(v + 1)^2(\ln \left( \frac{r}{a} \right))^2 + (1 + 2v)(1 + v) \ln \left( \frac{r}{a} \right) + v(v - 1) + 1}} \]

**Equation S2-11.** The angular component of the yield stress for a material undergoing a uniaxial tensile test, in terms of the displacement field variables.

The general elastic stress-strain relationship for this system is shown below:

\[ \varepsilon_1 = \frac{\sigma_1 - v \sigma_2}{E} \]

**Equation S2-12.** The generic stress-strain relationship for the described system.

Using Equation S2-12 in combination with Equations S2-8 and S2-9, expressions for the yield strains, \( \varepsilon_{\gamma y} \) and \( \varepsilon_{\theta y} \), can be found:

\[ \varepsilon_{\gamma y} = \pm \frac{\sigma_y((1 - v)(v + 1) \ln \left( \frac{r}{a} \right) + 1 - v^2)}{E \sqrt{(v + 1)^2(\ln \left( \frac{r}{a} \right))^2 + (1 + 2v)(1 + v) \ln \left( \frac{r}{a} \right) + v(v - 1) + 1}} \]

**Equation S2-13.** The radial component of the yield strain for a material undergoing a uniaxial tensile test, in terms of the displacement field variables.
Equation S2-14. The angular component of the yield strain for a material undergoing a uniaxial tensile test, in terms of the displacement field variables.

\[
\varepsilon_{\theta} = -z \frac{d^2 w}{dr^2}
\]

Equation S2-15. The radial component of strain in terms of the displacement field variables.

\[
\varepsilon_{\theta} = -z \frac{d w}{r \, dr}
\]

Equation S2-16. The angular component of strain in terms of the displacement field variables.

Carrying out the differentiations on Equation S2-1 and substituting them into Equations S2-15 and S2-16 yields:

\[
\varepsilon_{r} = -\frac{4z w_{\text{max}}}{3a^2} \left( \ln \left( \frac{r}{a} \right) + 1 \right)
\]

Equation S2-17. Simplified radial component of strain in terms of the displacement field variables.
\[ \varepsilon_r = -\frac{4w_{\text{max}}}{3a^2} \ln\left(\frac{r}{a}\right) \]

Equation S2-18. Simplified angular component of strain in terms of the displacement field variables.

Now, Equations S2-10, 11, 13, 14, 17, and 18 can, with careful attention paid to ensure the signs reflect reality, be substituted into Equation S2-4 to yield:

\[
\frac{U_{ey+p}}{V} = -\frac{\sigma_y(1-v^2)((v+1)((\ln\left(\frac{r}{a}\right))^2 + \ln\left(\frac{r}{a}\right)) + \frac{1}{2})}{E((v+1)^2(\ln\left(\frac{r}{a}\right))^2 + (1+2v)(1+v)\ln\left(\frac{r}{a}\right) + v(v-1) + 1)} + \frac{8\zeta \sigma_y W_{\text{max}}((v+1)((\ln\left(\frac{r}{a}\right))^2 + \ln\left(\frac{r}{a}\right)) + \frac{1}{2})}{3a^2 \sqrt{(v+1)^2(\ln\left(\frac{r}{a}\right))^2 + (1+2v)(1+v)\ln\left(\frac{r}{a}\right) + v(v-1) + 1}}
\]

Equation S2-19. Strain energy per unit volume at a point in the plate that has undergone plastic deformation.

While this equation describes the strain energy per unit volume at a point that has plastically deformed, there will be regions that are still in the process of elastic deformation. An equation that gives the strain energy per unit volume in an elastic region, \( \frac{U_{\text{elastic}}}{V} \), can be found by substituting equations S2-8, 9, 17, and 18 into Equation S2-2:

\[
\frac{U_{\text{elastic}}}{V} = \frac{16w_{\text{max}}}{(1-v^2)a^4} z^2 ((v+1)((\ln\left(\frac{r}{a}\right))^2 + \ln\left(\frac{r}{a}\right)) + \frac{1}{2})
\]
Equation S2-20. Strain energy per unit volume at a point in the plate that has undergone elastic deformation.

Now that expressions for the strain in areas of both plastic and elastic deformation, Equations S2-19 and S2-20, respectively, have been obtained, they can be integrated over the total volumes experiencing plastic and elastic deformation respectively to attain $U_{total}$. Given that the system is axisymmetric, the function delineating the region where the deformation is elastic (closer to the neutral surface of the plate) from the region where deformation is plastic (closer to the top or bottom of the plate), will return a $z$ coordinate for a given $r$ coordinate and exclude $\theta$. This two-dimensional “yield line” can be found by rearranging the combination of equations (5), (8), and (9):

$$z_y(r) = \pm \frac{\sigma_y a^2(1 - v^2)}{4Ew_{max}}((v + 1)^2(ln\left(\frac{r}{a}\right))^2$$

$$+ (1 + 2v)(1 + v) ln\left(\frac{r}{a}\right) + v(v - 1) + 1)^{-\frac{1}{2}}$$

Equation S2-21. The “yield line” for the displacement of a clamped plate.

This yield line function can then be used in the limits of the integral along the $z$ axis for $U_{total}$. For the region of plastic deformation, the limits will be $z_y$ and the surface of the plate ($t/2$), where $t$ is thickness. For the region of elastic deformation,
the limits will be the neutral surface \( (0) \) and \( z_y \) for the elastic region. Under the assumptions of Kirchhoff-Love plate theory, the material behaves the same way under tension and compression and stress is symmetric across the neutral plane. This allows for \( U_{total} \) to be calculated by doubling the integration over the top half of the plate, rather than integrating over its full volume. This simplifies the final equation. After completing the integrals in the \( z \) axis, the result must integrated through \( \theta \) and \( r \). The integral has the following form:

\[
\int_{V_{plastic}} \frac{U_{plastic}}{V} + \int_{V_{elastic}} \frac{U_{elastic}}{V} = U_{total}
\]

\[
= \int \int \int \left( \frac{1}{2} \int_{z_y(r)}^{t} \frac{\sigma_y \left( 1 - v^2 \right)}{E \left( (v + 1)^2 \left( \frac{r}{a} \right)^2 + (1 + 2v)(1 + v) \ln \left( \frac{r}{a} \right) + v(v - 1) + 1 \right)} r dz + \frac{8z\sigma_y w_{max} \left( (v + 1) \left( \ln \left( \frac{r}{a} \right) \right)^2 + \ln \left( \frac{r}{a} \right) + \frac{1}{2} \right)}{3a^2 \left( (v + 1)^2 \left( \ln \left( \frac{r}{a} \right) \right)^2 + (1 + 2v)(1 + v) \ln \left( \frac{r}{a} \right) + v(v - 1) + 1 \right)} \right) r dz \right. 
\]

\[
+ \left( 2 \int_{0}^{z_y(r)} \frac{16w_{max}^2 E}{(1 - v^2)a^4} Z^2 \left( (v + 1) \left( \ln \left( \frac{r}{a} \right) \right)^2 + \ln \left( \frac{r}{a} \right) + \frac{1}{2} \right) r dz \right) d\theta dr
\]

Equation S2-22. Total integrated strain energy for the deflection of a clamped plate.
Note the need to multiply the entire function by $r$ when integrating in cylindrical polar coordinates. The integrals in $z$ and $\theta$ are analytically solvable, however the integral in $r$ is not. This is reflected in the final form of the equation:

$$U_{total} = \pi \int_0^a r \alpha(r) \left( \frac{\sigma_y^3 a^2 (1 - v^2)^2}{3E^2 \omega_{max}} (\beta(r))^{-\frac{3}{2}} - \frac{2t(1 - v^2)\sigma_y^2}{E} (\beta(r))^{-1} \right. \left. + \frac{4t^2 \sigma_y \omega_{max}(1 - v^2)}{3a^2} (\beta(r))^{-\frac{1}{2}} \right) \, dr$$

$$\alpha(r) = (v + 1)((\ln \left(\frac{r}{a}\right))^2 + \ln \left(\frac{r}{a}\right)) + \frac{1}{2}$$

$$\beta(r) = (v + 1)^2(\ln \left(\frac{r}{a}\right))^2 + (1 + 2v)(1 + v) \ln \left(\frac{r}{a}\right) + v(v - 1) + 1$$

**Equation S2-23. Simplified total integrated strain energy for the deflection of a clamped plate.**

As this is not analytically solvable, it must be integrated numerically to get $U_{total}$. For this we used the “integral” function in MATLAB.

However, when yield stresses exceed certain values, the entirety of the surface of the plate may not have yielded. In this case the integral must be split into five separate integrals using the coordinates of the two intersections between the yield line ($z_y$) and the surface of the plate $t/2$, $r_1$ and $r_2$, as new limits:
\[
U_{\text{total}} = \pi \int_0^{r_1 (Z_y=\frac{t}{2})} r \alpha(r) \left( \frac{\sigma_y^2 a^2 (1 - v^2)^2}{3E^2 w_{\text{max}}} (\beta(r))^{-\frac{3}{2}} \right) dr
\]

\[
+ \pi \int_{r_1 (Z_y=\frac{t}{2})}^{r_2 (Z_y=\frac{t}{2})} r \alpha(r) \left( \frac{4w_{\text{max}}^2 Et^3}{3(1 - v^2)^2 a^4} \right) dr
\]

\[
+ \pi \int_{r_2 (Z_y=\frac{t}{2})}^{a} r \alpha(r) \left( \frac{\sigma_y^2 a^2 (1 - v^2)^2}{3E^2 w_{\text{max}}} (\beta(r))^{-\frac{3}{2}} \right) dr
\]

\[
+ \pi \int_0^{a} r \alpha(r) \left( \frac{t^2 \sigma_y w_{\text{max}} (1 - v^2)^2}{3a^2} \left( \beta(r) \right)^{-\frac{1}{2}} \right) dr
\]

\[
+ \pi \int_0^{r_1 (Z_y=\frac{t}{2})} r \alpha(r) \left( \frac{2\sigma_y^3 a^2 (1 - v^2)^2}{3E^2 w_{\text{max}}} (\beta(r))^{-\frac{3}{2}} - \frac{2t(1 - v^2) \sigma_y^2}{E} (\beta(r))^{-1} \right) dr
\]

\[
+ \frac{4t^2 \sigma_y w_{\text{max}}}{3a^2} (\beta(r))^{-\frac{1}{2}} dr
\]

\[
+ \pi \int_{r_2 (Z_y=\frac{t}{2})}^{a} r \alpha(r) \left( \frac{2\sigma_y^3 a^2 (1 - v^2)^2}{3E^2 w_{\text{max}}} (\beta(r))^{-\frac{3}{2}} - \frac{2t(1 - v^2) \sigma_y^2}{E} (\beta(r))^{-1} \right) dr
\]

\[
+ \frac{4t^2 \sigma_y w_{\text{max}}}{3a^2} (\beta(r))^{-\frac{1}{2}} dr
\]

\[
\alpha(r) = (v + 1)(\ln \left( \frac{r}{a} \right))^2 + \ln \left( \frac{r}{a} \right) + \frac{1}{2}
\]
\[
\beta(r) = (v + 1)^2 (\ln \left( \frac{r}{a} \right))^2 + (1 + 2v)(1 + v) \ln \left( \frac{r}{a} \right) + v(v - 1) + 1
\]

**Equation S2-24.** Total integrated strain energy for the deflection of a clamped plate for the special case where only some portions of the plate have yielded.

As this integral is also not analytically solvable, it must be integrated numerically to get \( U_{\text{total}} \). In order to solve it the “integral” function in MATLAB. Using equations (23) and (24), the total strain energy of the system can be obtained for arbitrary input parameters. This can be compared with the VdW energy for the same input parameters to determine if the specified deformation can be brought about by the action of VdW forces between the plate and the substrate (see below).

### 2.6.7. Calculation of van der Waals Interaction Energy Between a Nanoplate and a Substrate

The equation for the Van der Waals interaction energy per unit area between a plate of thickness \( t \) and a substrate of effectively infinite thickness is as follows:\(^{174}\)

\[
U_A = -\frac{A}{12\pi} \left( \frac{1}{d^2} - \frac{1}{(d + t)^2} \right)
\]

**Equation S2-25.** The van der Waals interaction energy between a plate of thickness, \( t \), and an infinitely thick substrate.
where $U_A$ is the VdW interaction energy per unit area, $A$ is the Hamaker constant for the system, and $d$ is the separation between the plate and the substrate. To calculate the overall Hamaker constant for the system of a triangular silver nanoplate interacting with a silicon substrate across a generic ligand layer containing a carbon chain we used the following equation:

$$A_{123} \approx (\sqrt{A_{11}} - \sqrt{A_{22}})(\sqrt{A_{33}} - \sqrt{A_{22}})$$

**Equation S2-26. Calculation of the Hamaker constant for two materials interacting through a medium.**

where $A_{123}$ is the Hamaker constant for medium 1 interacting with medium 3 through medium 2, and $A_{11}, A_{22},$ and $A_{33}$ are the Hamaker constants for the media 1, 2 and 3 respectively. $A_{Ag} = 38.50 \times 10^{-20}$ J, $A_{Si} = 18.65 \times 10^{-20}$ J, and $A_{ligand} \approx 5 \times 10^{-20}$ J. Therefore $A_{Ag-ligand-Si} \approx 8.26 \times 10^{-20}$ J. In order to obtain the total energy of interaction we must multiply Equation S2-25 by the area of the nanoplate. Assuming the triangular nanoplate has edges 1 $\mu$m in length, the total area is $4.33 \times 10^{-13}$ m$^2$.

Incorporating this information into Equation S2-25 we have:

$$U_{vdw} = -\frac{8.26 \times 10^{-20}}{12\pi} \left(\frac{1}{d^2} - \frac{1}{(d+t)^2}\right) \times 4.33 \times 10^{-13}$$

**Equation S2-27. The total van der Waals interaction energy in joules between a silver nanoplate and a silicon substrate through a carbonaceous surface ligand medium.**
where \( U_{vdw} \) is the total VdW interaction energy (in Joules) for a triangular silver nanoplate of thickness \( t \) (in meters) with edges length 1 um, separated by a ligand layer of thickness \( d \) (in meters) from a silicon substrate.

2.6.8. Estimating \( \sigma_y \) from Experimental Data

In an experimental scenario, due to the conservation of energy, the VdW interaction energy of a nanoplate must be equal to the strain energy of the deformation it is experiencing. Using this information, if we input the measured experimental parameters for \( a \) (50 nm), and \( w_{max} \) (15 nm) and assume \( \nu = 0.37 \) and that \( E = 102 \text{ GPa} \) (this is a mid-range value of \( E \) for silver nanoparticles, which varies between \(~90 \text{ and } 115 \text{ GPa} \))\(^{157-160}\), then a value for \( \sigma_y \) can be extracted. Because the spacing (d) between the nanoplate and substrate is difficult to obtain, we calculated \( \sigma_y \) for \( d = 1, 1.5, \) and \( 2 \) nm. The values of \( \sigma_y \) are 708, 235, and 120 MPa respectively. These \( \sigma_y \) values are significantly elevated over the bulk \( \sigma_y \) of \(~54 \text{ MPa} \). This is in agreement with previous experimental measurements of yield stress for silver nanoparticles which also demonstrate elevated values on the order of 1 GPa.\(^{161}\)

2.6.9. Comparing van der Waals Interaction Energy and Strain Energy

To visualize how VdW forces become strong enough to mechanically deform a triangular silver nanoplate of low enough thickness, we graphed the strain energy and VdW interaction energy against thickness on the same plot and observed the intersection of the two curves. In order to do this, experimentally observed input
parameters were used: $a = 50$ nm, $w_{max} = 15$ nm, as well as $d = 2$ nm (an estimate of ligand layer thickness). The material properties predicted above were used: $\nu = 0.37$, $E = 102$ GPa, and $\sigma_y = 120$ MPa. Using these inputs, and leaving $t$ as a variable, we used Equations S2-24 and Equation S2-27 to generate the plot in the main text Figure 2-1a. This is shown again in Figure S2-8.

![Plot of strain energy and VdW energy against nanoplate thickness. $w_{max} = 15$ nm, $a = 50$ nm, $d = 2$ nm.](image)

Figure S2-8. Plot of strain energy and VdW energy against nanoplate thickness. $w_{max} = 15$ nm, $a = 50$ nm, $d = 2$ nm.

In order to demonstrate that Van der Waals forces are generally capable of deforming silver nanoplates, and that the input values shown above are not the only ones for which this is true, we have generated plots of the same form as main text
Figure 2-1, but with different yet still realistic input parameters (Figures S2-9, S2-10, S2-11). Using these it can be seen how the thickness at which a 1 μm edge length triangular silver nanoplate becomes deformable by VdW forces changes based on the input parameters.

![Graph](image)

**Figure S2-9.** Plot of strain energy and VdW energy against nanoplate thickness. \( w_{\text{max}} = 15 \text{ nm}, \ a = 20 \text{ nm}, \ d = 2 \text{ nm}. \)
Figure S2-10. Plot of strain energy and VdW energy against nanoplate thickness. $w_{\text{max}} = 15 \text{ nm}, a = 50 \text{ nm}, d = 4 \text{ nm}$.

Figure S2-11. Plot of strain energy and VdW energy against nanoplate thickness. $w_{\text{max}} = 30 \text{ nm}, a = 50 \text{ nm}, d = 2 \text{ nm}$.
2.6.10. Applicability of Theory to Other Materials

This theory can be applied to other materials if valid material properties can be obtained for them. As a demonstration we carried out the calculation for SiO$_2$ ($\sigma_y = 155$ MPa, $v = 0.19$, $E = 74.8$ GPa, $A_{SiO_2} = 6.55 \times 10^{-20}$ J).$^{175,176}$ This is shown in Figure S2-12 which shows that for the same degree of deformation as previous examples, an SiO$_2$ nanoplate would need to be thinner.

![Graph showing energy of deformation for SiO$_2$ nanosheet of variable thickness.](image)

**Figure S2-12.** Energy of deformation for a SiO$_2$ nanosheet of variable thickness.

Another example is CdSe ($\sigma_y = 8.55$ GPa, $v = 0.345$, $E = 61.2$ GPa, $A_{CdSe} = 6.208 \times 10^{-20}$ J).$^{177,178}$ This is shown in Figure S2-13, which shows that a CdSe nanoplate would need to be less < 1 nm in thickness to be deformed by VdW forces.
according to the input parameters used. Incidentally, CdSe nanosheets of 0.9 nm in thickness have previously been synthesized and display flexibility.\textsuperscript{179}

**Figure S2-13. Energy of deformation for a CdSe nanosheet of variable thickness.**

**2.6.11. FEM and Solid Mechanics Calculations**

The analytical Kirchhoff-Love theory used in this work and described in detail above is strictly applicable when plate deformations are small compared to the plate thickness $t$. In addition, our analytical modeling also assumes that the sphere-plate contact is approximated as a point load at $r = 0$. We verified that these two assumptions provide reasonably accurate models for our experiments by using steady-state finite-element method (FEM) calculations (COMSOL Multiphysics with
the Nonlinear Solid Mechanics module) to determine the axisymmetric deformations of a silver nanoplate around an iron oxide template particle. The FEM simulations do not assume that deformations are small, and do not assume a point contact. To facilitate comparison with the Kirchhoff-Love theory that leads to the displacement field of Equation S2-1, van der Waals forces are not included in the simulation, and both materials in the calculation are taken to be elastic, homogeneous, and isotropic. Note that the assumption of elastic deformation is expected to fail because significant plastic deformation occurs due to stresses exceeding the yield stress, as discussed above. Here, we consider only elastic deformation to focus on the comparison with basic Kirchhoff-Love theory; the unrealistically large stresses observed in the simulation results indicate that plastic deformation occurs in the experiment.

In the FEM calculations, the nanoplate has an initial (i.e. undeformed) thickness of $t_0 = 9$ nm, and the iron oxide sphere has an initial diameter of $d_0 = 15$ nm. The nanoplate is clamped at the points $(r, z) = (a, 0)$ and $(a, t_0)$. The iron oxide particle rests below the nanoplate in an undeformed state. To initiate deformation, the sphere is displaced in the axial direction with a prescribed displacement $w = d_0$ for all points on the surface of the sphere. After this displacement, the bottom point on the sphere lies in the same $z = 0$ plane as the clamped bottom edge of the plate. This configuration represents the experimental scenario where both the template particle and the clamped portions of the nanoplate are supported by the substrate at the $z = 0$ plane. Note that the substrate itself is not necessary to include in our FEM
models because the VdW forces are not considered, and the nanoplate is clamped at $r = a$.

The contact between the sphere and nanoplate is calculated in a self-consistent manner along with the displacements, stresses, and strains in both materials. The contact surface is assumed to be frictionless, and no adhesion forces are considered. In the scenario where displacements at the contact are sufficiently small, our FEM contact modelling reproduces the results of classic Hertzian contact theory; deviations from Hertzian theory arise when the contact radius is not negligibly small compared to $d_0$. To avoid numerical difficulties associated with the nonlinearities in contact mechanics problems involving large displacements, we employ parametric sweeps over different template particle displacements and ensure that all results are converged with respect to the spatial mesh.

To compare the deflection fields against the experimental results and to generate stress profiles to understand the mechanical stress induced by the deformation, we performed several simulations of the experimental geometry in which a sphere deforms a clamped nanoplate disc. Also, for each simulation we have characterized the contact radius between the sphere and the nanoplate; we found that the value of the contact radius stays relatively stable across different geometric and material parameters. Additionally, to prove that VdW forces are necessary to achieve the deformed structures we observe experimentally, we also modelled the same sphere deforming a large triangular nanoplate, clamped at the edges. For every configuration we performed simulations using both the bulk Young’s modulus, 74
GPa, as well as an elevated Young’s modulus, 125 GPa, a phenomenon that is typically associated with nano-silver. Note that in all cases, the stresses required to achieve deformation exceed even an elevated yield stress value for nano-silver (~1 GPa), indicating the plastic deformation would occur in the experiment.

2.6.11.1. Simulations of a 75 nm Radius Disc

![Simulation of clamped disc with bulk Young’s Modulus, 74 GPa. (a) Surface stress map of deformed clamped disc and (b) plot showing the contact radius between the sphere and disc.](image)

![Simulation of clamped disc with elevated Young’s Modulus, 125 GPa. (a) Surface stress map of deformed clamped disc and (b) plot showing the](image)
contact radius between the sphere and disc. Panel (a) can be found as a component of Figure 2-3 in the main text.

2.6.11.2. Simulations of a 50 nm Radius Disc

*Note that for this set of simulations, the maximum displacement is 10 nm. Results for higher displacement values would not converge in COMSOL, due to the large stresses and strains.

Figure S2-16. Simulation of clamped disc with bulk Young's Modulus, 74 GPa. (a) Surface stress map of deformed clamped disc and (b) plot showing the contact radius between the sphere and disc.
2.6.11.3. Simulations of a 1 µm Edge-Length Nanoplate for Bulk Young’s Modulus Values

Figure S2-17. Simulation of clamped disc with elevated Young’s Modulus, 125 GPa. (a) Surface stress map of deformed clamped disc and (b) plot showing the contact radius between the sphere and disc.

Figure S2-18. Surface stress map of clamped nanoplate with bulk Young’s Modulus, 74 GPa.
2.6.11.4. Simulations of a 1 μm Edge-Length Nanoplate for Elevated Young’s Modulus Values

*Note that for this set of simulations, the maximum displacement is 10 nm. Results for higher displacement values would not converge in COMSOL.
Figure S2-20. Surface stress map of clamped nanoplate with elevated Young's Modulus, 125 GPa.

Figure S2-21. Total displacement map of clamped nanoplate with bulk Young's Modulus, 74 GPa.
Chapter 3

Surface Ligands Dictate the Mechanical Properties of Inorganic Nanomaterials

3.1. Abstract

The ability for surface ligand chemistry to influence the physical properties of inorganic nanomaterials is well-appreciated for optoelectronic phenomena but poorly understood for mechanical behavior. By screening a range of surface-bound molecules, we show that varying the particle-ligand bond enthalpy changes the mechanical strength of a silver nanoplate. A continuum model for plate deformation is developed in which the plate interior is considered bulk-like while a several atom-thick shell represents the surface atoms and adopts ligand-dependent yield strength. Electron diffraction experiments reveal that, relative to the core, atoms in the shell

\[ \text{Material in this chapter will appear as a peer-reviewed article in a subsequent publication.} \]
undergo lattice contraction or expansion as large as 7 and 14\%, respectively, contingent on the binding chemistry. These atomic distortions are responsible for changing surface stresses that give rise to the large changes in effective mechanical properties observed for entire particles. These results demonstrate size-dependent coupling between chemistry and mechanics at the nanoscale, allowing for dynamic restructuring of nanoparticle shape through ligand coordination.

3.2. Introduction

Nanoscience is built on the principle that unique properties arise at small length scales. Such phenomena can develop from a wide variety of factors including quantum confinement, changing reactivity, or an increased proportion of surface atoms, all of which fundamentally relate to a coupling between two distinct properties. A coupling that is negligible for bulk materials but becomes potent at the nanoscale. For example, novel optical properties arise in quantum dots from size-dependent coupling between photons and excitons, while catalytic behavior can be explained through by the coupling of crystal size/shape and surface energy.\textsuperscript{127, 180-184} It is known that the mechanical behavior of inorganic materials is also heavily size-dependent\textsuperscript{145} – where the elastic deformation of a structure has an exponential dependence on material thickness. This implies that for sufficiently small systems, mechanical behavior may be coupled to other physical factors whose influence would be trivial for macroscopic materials. In this work we show the chemistry of surface ligand adsorption, a ubiquitous phenomenon in colloidal nanoscience, controls the
global mechanical properties of nanoparticles with at least one dimension below ~20 nm. This effect arises from the ability of a surface-bound molecule to alter the sign and magnitude of intrinsic surface stress in a nanocrystal, an effect that is augmented by a high fraction of surface atoms. This finding challenges the conventional depiction of nanoparticles as static, rigid objects and instead demonstrates their ability to be mechanically transformed via surface chemistry.

The physical consequences of molecular adsorption to metal surfaces have been investigated primarily by two scientific communities – molecular sensing and surface science. The former studies the bending of microcantilevers in response to adsorbate binding - an effect attributed to changes in surface stress, or the work required to elastically stretch a surface. This understanding derives from a continuum-scale perspective, overlooking the details of atomic reorganization and chemisorption.\textsuperscript{4, 7, 14, 21, 24, 28, 32, 39, 46, 54, 55, 62, 63} The latter community experimentally probes angstrom-level shifts in atomic positions in bare and decorated surfaces, but rarely connects these processes to global mechanical properties of the material.\textsuperscript{2, 3, 64-66, 69, 70, 78, 109} Understanding ligand-driven mechanics in inorganic structures at the nanoscale represents an opportunity to reconcile the observations made in each of the previously described fields, it exists in the intermediate between the atomic and macroscale.

Although historically the identity of surface ligands on nanomaterials has been considered mostly in the context of colloidal stability and functionalization,\textsuperscript{131, 185}
there is a growing appreciation for the ability of ligands to influence or even control certain properties. For example, it has been observed that surface ligands can change the photoluminescence of quantum dots (QDs) and noble metal nanoclusters by eliminating surface traps and reducing non-radiative relaxation pathways.\textsuperscript{124-126} Additionally, it has been shown that different ligand chemistries can change the complete crystallographic structure of thin gold nanosheets and modulate metal interatomic distances in nanoparticles and nanoclusters.\textsuperscript{67,115-120,123,186} Despite these advances, the connection between ligands chemistry and nanoparticle mechanics remains unclear.

Here we demonstrate a fundamental, size-dependent nanoscale coupling between chemistry and mechanics, where the binding of surface ligands modulates the inherent mechanical strength of an inorganic nanoparticle (Figure 3-1). Nanoscale systems are ideal for interrogating this phenomenon, as the role of surface chemistry is enhanced due to the increased ratio of “surface-like” to “bulk-like” atoms.\textsuperscript{104, 114, 121, 122} We observe that nanoplates with strongly interacting ligands display a greater mechanical strength than their counterparts with weakly interacting ligands (Figure 3-1a and b). We propose that this shift in mechanical properties is a direct consequence of the surface stress induced by atomic reorganizations upon ligand interaction (Figure 3-1c through e).
Figure 3-1. Thin silver nanoplates have a (a) low mechanical strength or (b) high mechanical strength depending on the surface chemistry. The binding of a ligand, L, to the surface (c) relieves the intrinsic tensile stress of a silver surface, but (d) with increasing binding strength induces compressive stress and atomic reorganization. Atoms are colored from a gray to blue gradient indicating the gradual transition from “bulk-like” to “surface-like” behavior of a surface. (e) Commonly used capping moieties used in nanoparticle synthesis and in this study in order of increasing binding strength.

3.3. Results and Discussion

To explore the impact of surface ligands on nanoparticle mechanics we optimized the synthesis of ultra-high aspect ratio triangular silver nanoplates ~8 nm in thickness and hundreds of nanometers on an edge. Previous work has demonstrated that nanoplates of these dimensions are extraordinarily flexible and can deformed over small spherical template particles (Figure 3-2a). Measurement
Figure 3-2. Thin silver nanoplates are (a) readily deformable over small spherical template particles, the result of which is a distinctive bend contour, the diameter of which relates to the lateral extent of the deformation. (b) These nanoplates can be decorated with a wide range of commonly used ligands of increasing strength, (c) the consequence of which is an increase in then bend contour diameter for a single template particle size. (d) A plot of the ligand bond enthalpies versus bend contour diameter reveals a proportional relationship that holds true for several template sizes (Table S3-2).
of the diameter of bend contours caused by this deformation can be used to extract their effective mechanical constants. Here, an increasing bend contour size implies nanoplates that are less mechanically compliant. We screened the effect of surface functionalization with several other ligands, varying in their binding strength (Figure 3-2b). We hypothesized that plates synthesized under identical conditions but decorated with surface ligands of increasing binding strength would result in differential mechanical strength as measured by larger bend contour diameters.

The as-synthesized nanoplates are capped with a weakly bound citrate ligand and used as a mechanical benchmark and compared against nanoplates decorated with a library of other commonly-used nanoparticle ligands of increasing strength: pyrrolidone (monomer of PVP), bis(p-sulfonatophenyl)phenylphosphine (BSPP), a PEG-thiol, and an adamantyl-substituted n-heterocyclic carbene (NHC) (Figure 3-2b). It was observed that the diameter of the bend contour increased proportionally with the binding strength of the surface ligand upon deformation over a 15 nm template particle (Figure 3-2c and d). These results were plotted as a function of ligand bond enthalpy, showing a direct relationship.2, 52, 188-190 This experiment was repeated for several template particle sizes, and the observed trend persisted across all samples. It is also noted that for a single ligand chemistry, the diameter of the bend contour also increased with template size (Table S3-2). These data serve as further confirmation that the extent of the bend contour is directly related to the spatial extent of the deformation, where a larger template particle size will result in a larger deformation area. This TEM characterization of the bend contours was corroborated
by AFM measurement, which shows topographically, that the lateral extent of the bend contour is proportional to ligand binding strength for a single template size (Figure S3-5).

Further experiments were performed to determine if the ligand binding strength is the dominant contribution to the modulation of mechanical strength in nanoplates, by exploring other potential influences. It has been observed that under sub-monolayer ligand conditions, side chain interactions can influence induced surface stress,24,45,51,54,191 which for the purposes of this study, could influence the nanoplate mechanical behavior. It is also well known that ligands pack on metal surfaces in different configurations and overlayers, each of which has a packing density associated with it.3,52 To determine whether these factors contributed to our observations, we studied both side chain interactions and ligand packing density. To explore side-chain interactions, TEM measurements were collected for deformed nanoplates functionalized with PEGylated thiol ligands of different lengths, as well as a thiol ligand with a less conventional side chain chemistry, a crown ether. It was observed that each of thiol ligands produced identical bend contour measurements compared to each other, regardless of side chain length or moiety (Figure S3-6). This suggests that side chain interactions did not contribute to the differential mechanical behavior of nanoplates. To quantify the packing densities of each ligand used, inductively coupled plasma (ICP) mass spectrometry (MS) was employed to determine the concentration of silver nanoparticles and thermogravimetric analysis (TGA) measurements yielded ligand molecule concentrations – which when
combined yield a ligand footprint in ligands/nm². The results revealed that the binding density across all ligands used was relatively similar, and any trend present did not follow the mechanical behavior of differently functionalized plates (Figure S3-7, S3-8, Scheme S3-1, Table S3-3). Based on an understanding of how self-assembled monolayers (SAMs) can pack on surfaces, it is assumed that each ligand packs at its maximum density under the experimental conditions. These experiments in combination, exclude ligand-ligand interactions as well as density as factors that contribute to the trends in bend contour diameter that are observed. This further validates that the primary source of variable nanoplate mechanical strength is the ligand binding chemistry.

On a macroscopic scale, it is apparent that some atomic-scale interaction at the ligand-surface interface results in changing mechanical behavior. Therefore, the nanoplate and its surface can be viewed as a simplified core/shell model, where the *core atoms* in the center of the nanoplate lattice display bulk-like behavior and the *shell atoms* correspond to a few atomic layers at the surface (Figure 3-3a). Using the analytical modelling from our previous work,¹⁸⁷ we adjusted the geometry to account for this core-shell model, where core atoms displayed bulk silver properties, and shell atoms (corresponding to 2 atomic layers) could exhibit variable mechanical properties. To achieve the experimental bend contour geometries observed, the model showed that the surface yield stress must increase with ligand strength for the strain and the van der Waals energies to converge appropriately. The model predicts that the surface yield stress must range from 234 to 315 MPa with increasing ligand
strength (Figure 3-3b). While this is much higher than the bulk yield stress of 54 MPa, the shell atoms in these calculations account for a 10% contribution to the total yield stress of the nanoplate. Calculated by weighted average, this increase in the surface yield stress results in effective total yield stresses ranging from 72.0 to 80.1 MPa (Figure 3-3b). When these results are plotted against reported ligand bond enthalpies, a linear relationship is observed suggesting that for these geometries there is a linear coupling constant of 1.17 MPa change in the surface yield stress per kJ*mol$^{-1}$ increase in bond enthalpy (Figure 3-3c).

Figure 3-3. Silver nanoplates can be understood as (a) a core-shell structure, where shell atoms are undergoing surface chemistry influences. (b) When
modelled as such, this model shows the surface yield strength of nanoplates must increase with ligand binding strength. (c) The yield stress of the shell and the effective nanoplate yield stress both display a linear relationship with the reported bond enthalpy of the ligand chemistries explored. (d) This surface effect shows the expected size dependence, where the thickness of the nanoplate changes the sensitivity of the system to shell, or surface, effects.

If this effect can truly be interpreted as a core/shell relationship, then the mechanical response to surface chemistry should be size dependent – changing the thickness of the nanoplate does not change the surface atom-ligand interaction, but only changes the fraction of core atoms. To test this size dependence, nanoplates of different thicknesses were synthesized and deformed over template particles for the cases of citrate and thiol ligand chemistries (Figure 3-3d). For each nanoparticle thickness, the general trend with changing surface chemistry holds true: thiol-capped nanoplates produce a larger bend contour than their citrate-capped counterparts. However, the overall change in bend contour size corresponding to the change in surface chemistry increases as nanoplate thickness decreases. In other words, the smaller the fraction of core atoms comprising the overall nanoplate volume, the more sensitive the system is to shell effects. In fact, the data shows that just beyond a thickness of 20 nm, the two traces of ligand chemistries would converge, suggesting that the shell effect would become negligible. It should be noted that this deformation geometry results in plastic deformation as the main contributor to the calculated strain energy.\(^{187}\) As a result, the yield stress is the main mechanical variable that can account for the differences observed between nanoplate samples. While it is probable
that the Young’s modulus is also affected by ligand chemistry and size effects,\textsuperscript{34, 39} this factor is negligible for under the existing experimental conditions. It is estimated by the model that elastic deformation accounts for $<10\%$ of the overall strain in the system. These results demonstrate how the mechanical behavior of nanoplates, appearing to be influenced by ligand chemistry, can be modelled by a continuum-level core-shell system.

While able to be modelled at a global scale, the effect of ligand chemistry is surely a local, atomic one. Despite the intricate nature of the interaction between adsorbates (ligands) and surfaces, it is well appreciated that upon ligand binding, surfaces restructuring and changes in surface stress occur. Most bare metal surfaces are under an intrinsic tensile surface stress due to undercoordination; surface atoms contract inwards towards the rest of the lattice to optimize their electronic environment. Upon ligand binding, this intrinsic surface stress is relaxed, and surface atomic positions are reorganized. For interactions of increasing strength, this atomic reorganization involves the introduction of surface compressive stresses and can even remove atoms from the lattice.\textsuperscript{3} These surface effects impact not only the primary surface atoms, but cause lattice distortions propagating inwards two to four atomic layers (Figure 3-1). For this nanoplate system, we employed a correlated electron diffraction experiment to probe the lattice spacings of differently functionalized nanoplates (Figure 3-4, Table S3-4). In a typical electron diffraction for silver nanoplates, the first order diffraction spots belong to a (220) family of planes, corresponding to a normal lattice spacing of 0.145 nm (Figure 3-4a and b). Since
surface atoms make up a non-negligible percentage of the thin nanoplates, ≥10%, lattice measurements from electron diffraction patterns for an entire nanoplate would show deviations from the expected values if large surface reorganizations exist. Lattice measurements were obtained for nine individual nanoplates when capped with citrate ligands and after exchange with thiol ligands (Figure 3-4c). On average, the citrate nanoplates showed a lattice contraction of 6.7%. For bare metal surfaces, lattice contractions of up to 15% and tensile surface stresses in the range of 4 N m⁻¹ have been observed.³ ⁶⁵ ⁶⁶ It is known that upon interaction with a weakly binding ligand, a portion of tensile surface stress is relieved. This is consistent with our findings, as the citrate interaction is weak. Once exchanged with thiol ligands, the nanoplates have an average lattice expansion of 11.8%, which is in good agreement with literature studies that have seen thiol-mediated expansions of up to 19% and induced compressive surface stresses of -5 N m⁻¹.⁷⁸ ¹⁰⁹ ¹²⁷ These lattice spacing data are plotted against the surface yield stress found via the analytical model in Figure 3. Linear interpolation of the relationship reveals that lattice spacings of -3.2% and +1.2% for the cases of pyrrolidone and the phosphine ligand, respectively (Figure 3-4d). This analysis unites the continuum level results obtained with the atomistic lattice spacing observations and the known bond enthalpies for the studied ligands.
Figure 3-4. Single-particle studies of nanoplates. The lattice spacing of (a) silver nanoplates can be determined by (b) measuring the $r$ spacing in a SAED pattern. (c) Single particle studies of this lattice spacing for citrate- and thiol-
capped nanoplates reveal a change in lattice spacing, as ligand-mediated atomic distortions take place. (d) The plot of surface yield stress versus lattice spacing allows for an estimation of the effect for other ligands. (e) Single-particle deformation studies also reveal the shape transformations of a deformed nanoplate upon step-by-step ligand exchanges, (f) which results in increasing bend contour diameter.

In the cantilever literature, the change in surface stress results in deflection, or a globally observable structural change. Recently, it has been shown that the strength of adsorption is related to the extent of cantilever deflection. This result is consistent with this study's demonstration of the relationships between ligand bond enthalpy, atomic reorganization, and stress. Here we present how our observations can be leveraged to change the shape of silver nanoplates. In order to achieve this, a correlated, single-particle TEM study was performed. A citrate-capped nanoplate was deformed over 15 nm templates, and a bend contour was identified and imaged. The sample was then incubated in solutions of increasingly strong ligands and imaged after each iteration (Figure 3-4e). After each step of ligand exchange, it was observed that the bend contour increased in diameter from 90-138 nm (Figures 3-4f, S3-9, S3-10). These data show that the shape of a nanoparticle can be dynamically restructured by ligand chemistry, further demonstrating that nanoscale objects are not static objects, but rather are subject to structural changes via novel coupling between chemistry and mechanical properties.
3.4. Conclusion

This work joins the observations of the disconnected molecular sensing and surface science literature and demonstrates how chemistry-driven atomic perturbations can lead to global changes in material properties. Nanoscale objects are distinctively situated to study this phenomenon, as there is an enhanced ratio of surface to bulk atoms, rendering surface effects particularly influential. While important as a unifying work for the two aforementioned fields, it also has significant implications for the field of nanoscience. For decades, colloidal nanoparticles have been stabilized by surface ligands, but little has been understood about how the interaction between the two and is only now beginning to be illuminated. This new nanoscale mechano-chemical coupling not only changes our fundamental understanding of nanoparticle systems as a whole, but also provides a framework for future applications. Moreover, this work further changes the traditional notion of nanoparticles as static objects, clearly demonstrating a dynamic change in shape upon ligand exchange.

3.5. Funding Acknowledgement

M. R. J. would like to acknowledge financial support from the Robert A. Welch Foundation (Grant C-1954) and the David and Lucile Packard Foundation (Grant 2018-68049). S.M. R. would like to acknowledge financial support from a National
Science Foundation Graduate Research Fellowship #1450681. The authors would like to acknowledge financial support from Rice University.

3.6. Experimental Methods and Supporting Information

3.6.1. Chemicals and Materials

All chemicals were used as purchased with no further purification or processing. Trisodium citrate (Na$_3$C$_6$H$_5$O$_7$ • 2H$_2$O, 99.0% ACS Reagent), silver nitrate (AgNO$_3$, 99.9999% trace metals basis), hydrogen peroxide (H$_2$O$_2$, 30% w/w in water ACS reagent with inhibitor), sodium borohydride (NaBH$_4$, 99.99% trace metals basis), L-ascorbic acid (C$_6$H$_8$O$_6$, 99.0% bioXtra), hydrochloric acid (HCl, >99.999%), nitric acid (HNO$_3$, >99.999%), deuterium oxide (D$_2$O, 99.9%), 2-pyrrolidone (C$_4$H$_7$NO, >99%), Silver standard for ICP (1000 mg/mL, TraceCert), Holmium standard for ICP (1000 mg/mL, TraceCert), Indium standard for ICP (1000 mg/mL, TraceCert), 1,3_Bis(1-adamantyl)imidazolium tetrafluoroborate (C$_{23}$H$_{33}$BF$_4$N$_2$, 97%), and potassium tert-butoxide solution (KO'Bu, 1.0 M in THF) were purchased from Sigma Aldrich. Acetonitrile (C$_2$H$_3$N, ChromAR) was purchased from Macron. The thiol molecules used for ligand studies, HS-C$_x$-(PEG)$_y$-COOH (x=6,11 , y=3,6 ) and 12-Crown-4-CH$_2$-O-CH$_2$-SH were purchased from Prochimia Surfaces. Bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (BSPP, >97%) was purchased from Strem Chemicals, Inc. Oleic acid capped
iron oxide nanospheres (15 nm) in chloroform were purchased from Ocean NanoTech.

3.6.2. Preparation of Silver Nanoplates

Silver nanoplates were prepared by modification of previously published protocols.\textsuperscript{150, 151} Seeds were prepared in an aqua regia-cleaned scintillation vial by combining fresh nanopure water (20 mL), trisodium citrate (1.2 mL, 75 mM), AgNO\textsubscript{3} (0.020 mL, 100 mM), and H\textsubscript{2}O\textsubscript{2} (0.048 mL, 30\% w/w) under vigorous stirring. To this, a freshly prepared solution of NaBH\textsubscript{4} (0.120 mL, 100 mM) was injected, and the reaction progressed over a 30-minutes as the solution turned from yellow to blue. The nanoprinseeds were stored on a benchtop at room temperature. To grow thin, high aspect ratio nanoplates, an aqua-regia cleaned scintillation vial in an ice bath, fresh nanopure water (10 mL), acetonitrile (5 mL), trisodium citrate (0.200 mL, 75 mM), and ascorbic acid (0.100 mL, 100 mM) were added under vigorous stirring. Meanwhile, an aliquot of the previously prepared seeds was subjected to centrifugation (10 minutes, 20133 rcf) to remove unreacted precursors. After the spin cycle, the supernatant was removed and the pelleted nanoprisms were concentrated 5x via resuspension in fresh nanopure water. These concentrated nanoplate seeds were immediately added to the reaction vial (0.035 mL), after which AgNO\textsubscript{3} (0.120 mL, 100 mM) was injected. This slow growth reaction proceeded to stir vigorously in the ice bath for approximately two hours, yielding a pale blue solution, before being moved to the refrigerator. After growth overnight, large thin silver nanoplates had visibly settled out of solution as a grey precipitate. Upon disturbing the precipitate, the
solution appeared to be blue with a grey pearlescent quality, indicating the presence of the large, light scattering nanoplates. Thicker nanoplates were achieved by adding less trisodium citrate to the growth solution. This provides less passivation of the (111) triangular faces and allows for more growth to occur along the thickness dimension. Thinner nanoprisms were achieved by adding fewer seed particles to the standard growth solution.

### 3.6.3. Ligand Exchange of Nanoplates

Grown nanoplates are natively capped with citrate ligands. To exchange citrate more strongly binding ligands for, a solution of the new ligand (0.100 mM final concentration) was added to nanoplates. This mixture was then subjected to constant agitation at 4°C overnight before use. *Ex situ* ligand exchange was performed when citrate-capped nanoplates were already deformed over template particles on TEM grids, by incubating the TEM sample in a solution of the new ligand (0.100 mM) for four hours.

### 3.6.4. Preparation of N-Heterocyclic Carbenes

The preparation of the NHC ligand was performed following a published protocol.\textsuperscript{192} The NHC precursor used for this study, 1,3-Bis(1-adamantyl)imidazolium tetrafluoroborate, was evacuated on a Schlenk line for an hour. Using a molar excess of a strong base, KO\textsubscript{t}Bu, the precursor was deprotonated over a dry ice/EtOAc bath (-78°C). This was then used as an NHC ligand stock solution, where ex-situ ligand exchange was performed with citrate-capped nanoplates.
3.6.5. Preparation of TEM and AFM Samples

Iron oxide nanospheres (0.001 mL) were freshly diluted into toluene (15 mL). Grown nanoplates were spun down (1 min) with a tabletop centrifuge, supernatant was removed, and the nanoplates were resuspended with an equal volume of nanopure water. To prepare a TEM sample, diluted iron nanoparticles (0.0035 mL) were drop cast onto a TEM grid and dried. Then, washed nanoplates (0.0065 mL) were drop cast onto the same grid and dried under vacuum. All BF, DF, and SAED TEM data were obtained with a JEOL 1230 High Contrast TEM operated at 80 kV. Size analysis from TEM images was done using ImageJ. To prepare AFM samples, diluted iron nanoparticles (0.015 mL) were drop cast onto a mica disc and dried under vacuum followed by washed nanoplates (0.030 mL). All AFM data were obtained with a Park NX20 AFM using tapping mode.

3.6.6. TGA Experiments

TGA analysis was performed using a Mettler Toledo/DSC 3+ system. A 30 mL volume of as-synthesized, or as-exchanged nanoplates were rinsed and concentrated by centrifugation to remove excess ligands. The concentrated nanoplates were then placed in a heated TGA pan to remove excess moisture before analysis. To analyze the mass of ligands in the sample, the TGA proceeded in three stages: a heating ramp from room temperature to 120°C at 20°C/min, where the temperature was held for 10 minutes, and finally a heating ramp to 1000°C at 10°C/min. This resulted in a mass loss around 350°C corresponding to the decomposition of organic molecules. This absolute mass loss was used to calculate the number of ligand molecules in 1 mL of nanoplate solution. For each
ligand, three separate TGA analyses were performed and averaged to account for any experimental heterogeneity in nanoplate preparation and subsequent ligand exchange.

3.6.7. ICP-MS Experiments

The ICP-MS protocol used here was adapted from previous literature. All analyses were carried out on a Perkin Elmer NexION 300 ICP-MS using an argon flow. Ag nanoplate samples were digested using aqua regia solution prepared by mixing HCl and HNO₃ in a 3:1 ratio. This aqua regia was diluted with water to 5% and used as a matrix for the ICP-MS solutions. Digested nanoplates were diluted 2000x by volume for analysis. The concentration of silver in digested nanoplate samples was determined by comparison to a five point standard curve comprised of known Ag concentrations prepared from an ICP silver standard: 1, 5, 10, 20, 30 ppb. The standard solutions were measured five times while the unknown samples were measured three times and averaged. A flush was performed in between each of the sample measurements and a blank was measured before and after all measurements were taken to ensure the validity of the measurements.

3.6.8. NMR Experiments

All NMR experiments were carried out using a Bruker 500 MHz NMR spectrometer. Experimental data presented in the main text is predicated on the assumption that ligand exchange goes to completion. To verify this, exchange between the two weakest ligands was examined. It was assumed that ligand exchange between the two weakest ligands would be the least favorable, and least likely to go to completion. Therefore, standard spectra of trisodium citrate and pyrrolidone in D₂O were collected. Then, citrate-
capped nanoparticles were synthesized in D$_2$O (100 mL scale) and subsequently washed and concentrated. This sample was then analyzed with NMR, and peaks corresponding to citrate were observed. This same process was repeated for nanoplates that had been exchanged for pyrrolidone. Pyrrolidone peaks were observed in the sample along with trace citrate peaks. The difference in intensity was used to determine the relative concentration of the ligands, and therefore, the exchange completion.

### 3.6.9. Experimental Supporting Figures, Tables, and Schemes

<table>
<thead>
<tr>
<th>Reported Size (nm)</th>
<th>Measured Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>11.0 ± 0.9</td>
</tr>
<tr>
<td>15</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>20</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>25</td>
<td>25 ± 1</td>
</tr>
<tr>
<td>30</td>
<td>30 ± 3</td>
</tr>
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Table S3-1. Size analysis of iron oxide template nanoparticles. Iron nanoparticles were sized concurrently with bend contour measurements.
Figure S3-1. Bar chart showing the average bend contour diameter for increasing ligand binding strength across varying template sizes. Replotted data that can be seen in main text Figure 1. Error bars represent standard deviation of the bend contour measurement and encompass the heterogeneity of the nanoplate sample.
<table>
<thead>
<tr>
<th>Ligand Chemistry</th>
<th>Template Size (nm)</th>
<th>Sample Size, n</th>
<th>Bend Contour Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate</td>
<td>10</td>
<td>107</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>313</td>
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</tr>
<tr>
<td></td>
<td>30</td>
<td>32</td>
<td>116</td>
</tr>
<tr>
<td>Pyrrolidone</td>
<td>10</td>
<td>97</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>204</td>
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</tr>
<tr>
<td></td>
<td>30</td>
<td>11</td>
<td>148</td>
</tr>
<tr>
<td>Phosphine</td>
<td>10</td>
<td>75</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>177</td>
<td>87</td>
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</tr>
<tr>
<td></td>
<td>30</td>
<td>15</td>
<td>172</td>
</tr>
<tr>
<td>Thiol</td>
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<td>76</td>
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</tr>
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<td></td>
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<td>35</td>
<td>199</td>
</tr>
<tr>
<td>NHC</td>
<td>10</td>
<td>29</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>16</td>
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<td>23</td>
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</tr>
<tr>
<td></td>
<td>30</td>
<td>8</td>
<td>226</td>
</tr>
</tbody>
</table>

Table S3-2. Data summary of bend contour measurements for all ligands and all template sizes.
Figure S3-2. The bend contour measurements are demonstrated to be statistically different from one another via a one-way Welch ANOVA test. This analysis was repeated for all samples to verify the statistical significance. Therefore, the error bars can be interpreted as reflective of the inherent heterogeneity between nanoplates. The sample data set shown is for deformation of a nanoplate over a 15 nm template particle.
Figure S3-3. Measurements of bend contour diameter for different substrates. These data demonstrate the lack of dependence of the behavior of nanoplates on substrate composition. These data were collected for deformation of a nanoplate over a 15 nm template particle.
Figure S3-4. Measurements of bend contour diameter for different template particles. These data demonstrate the lack of dependence of the behavior of nanoplates on template particle composition. Iron oxide nanoparticle templates are capped with oleic acid. Gold nanoparticle templates are capped with citrate. These data were collected for deformation of a nanoplate over a 20 nm template particle.
Figure S3-5. Topographical measurement of local deformation in nanoplates with varying ligand chemistry. The TEM data presented in Figure S1 and main text Figure 2 is validated by these AFM traces, which show an increase in the lateral extent of deformation with increasing ligand strength. The relationship between the bend contour measurement and these data is 0.79±0.06. These data were collected for deformation of a nanoplate over a 15 nm template particle.
Figure S3-6. Mechanical behavior of deformed nanoplates functionalized with thiols of various side-chain chemistries. It is demonstrated here that the bend contour size is independent of side-chain chemistry.
Figure S3-7. Ligand binding density results. The size of the bend contours is directly related to the ligand binding strength, but this trend does not correlate to binding density, suggesting that binding density is not an important factor in our observations. Additionally, all ligand binding densities are similar to one another, and are likely at maximal coverage.\textsuperscript{52} These data were gathered by determining the concentration of silver and organic ligands by ICP-MS and TGA, respectively, for each sample.
Figure S3-8. Representative TGA data for determining the concentration of ligands. Absolute mass loss was used to calculate the concentration of organic molecules in solution.

Scheme S3-1. Sample calculation flow of ligand density calculation based on concentration data from ICP-MS and TGA measurements. Green boxes and arrows show the logical flow of the calculation. Red boxes demonstrate data acquired by experiments. Unboxed plain text corresponds to constants or geometrically-calculated parameters.
Table S3-3. Summary of NMR ligand exchange data. Peaks shifted downfield for on-particle experiments suggest that ligands are indeed bound to nanoplate surfaces. After exchange, the relative integration of pyrrolidone to citrate peaks is 105:1. This corresponds to a relative concentration of pyrrolidone to citrate of 210:1, suggesting that ligand exchange goes to completion >99%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NMR peaks of interest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Citrate</td>
<td>quartet, 2.45 ppm</td>
</tr>
<tr>
<td>On-Particle Citrate</td>
<td>quartet, 2.82 ppm</td>
</tr>
<tr>
<td>Pyrrolidone</td>
<td>triplet, 3.29 ppm</td>
</tr>
<tr>
<td>Exchanged On-Particle Pyrrolidone</td>
<td>triplet, 3.55 ppm (int 105)</td>
</tr>
<tr>
<td></td>
<td>quartet, 2.82 ppm (int 1)</td>
</tr>
<tr>
<td>Free Citrate Pyrrolidone Concentration Mix</td>
<td>210:1</td>
</tr>
<tr>
<td></td>
<td>*Concentration ratio needed to achieve same relative integration</td>
</tr>
</tbody>
</table>

Table S3-4. Summary of single particle correlated measurements of lattice spacing. These data correspond to main text (Figure 3-4).
Figure S3-9. Ex-Situ ligand exchange on silver nanoplates. Pre-prepared TEM grids with citrate-capped nanoplates are incubated in a thiol solution. After this, the grid was rinsed, and bend contours were measured. The sample that was exchanged ex-situ (purple) had the similar bend contour measurement as nanoplates that were capped with thiols in solution (red).
Figure S3-10. Control experiments for the correlated ex-situ ligand exchange. Three separate bend contours from citrate-capped prisms were measured under different conditions: initial conditions (red), imaged after two hours (blue), and after the TEM sample grid was flipped over (green). Scale bars 20 nm. The consistency of the measured diameters suggests that the differences observed in main text Figure 4 are due to shape transformations by changing the nanoplate surface chemistry.
3.6.10. Continuum Scale Core-Shell Modelling

The theory used for the model described in this paper is based upon work in a previous publication, in which Equation S3-1 is numerically solved using the “integral” function in MATLAB to find the total strain energy ($U_{\text{total}}$) of the bending plate system.

\[
U_b = \pi \int_0^{r_1 \left( \frac{Z_y}{Z} \right)} r \alpha(r) \left( \frac{\sigma_y^3 a^2 (1 - v^2)^2}{3 E^2 w_{\text{max}}} \right) \left( \beta(r) \right)^{-\frac{3}{2}} \, dr + \pi \int_{r_1 \left( \frac{Z_y}{Z} \right)}^{r_2 \left( \frac{Z_y}{Z} \right)} r \alpha(r) \left( \frac{4 w_{\text{max}}^2 E t^3}{3 (1 - v^2)^2 a^4} \right) \, dr
\]

\[
+ \pi \int_{r_2 \left( \frac{Z_y}{Z} \right)}^{a} r \alpha(r) \left( \frac{\sigma_y^3 a^2 (1 - v^2)^2}{3 E^2 w_{\text{max}}} \right) \left( \beta(r) \right)^{-\frac{3}{2}} \, dr
\]

\[
+ \frac{t^2 \sigma_y w_{\text{max}} (1 - v^2)^2}{3a^2} \left( \beta(r) \right)^{-\frac{1}{2}} \, dr
\]

\[
+ \pi \int_0^{r_1 \left( \frac{Z_y}{Z} \right)} r \alpha(r) \left( \frac{2 \sigma_y^3 a^2 (1 - v^2)^2}{3 E^2 w_{\text{max}}} \right) \left( \beta(r) \right)^{-\frac{3}{2}} - \frac{2 t (1 - v^2) \sigma_y^2}{E} \left( \beta(r) \right)^{-1} \, dr
\]

\[
+ \frac{4 t^2 \sigma_y w_{\text{max}}}{3a^2} \left( \beta(r) \right)^{-\frac{1}{2}} \, dr
\]

\[
+ \pi \int_{r_2 \left( \frac{Z_y}{Z} \right)}^{a} r \alpha(r) \left( \frac{2 \sigma_y^3 a^2 (1 - v^2)^2}{3 E^2 w_{\text{max}}} \right) \left( \beta(r) \right)^{-\frac{3}{2}} - \frac{2 t (1 - v^2) \sigma_y^2}{E} \left( \beta(r) \right)^{-1} \, dr
\]

\[
+ \frac{4 t^2 \sigma_y w_{\text{max}}}{3a^2} \left( \beta(r) \right)^{-\frac{1}{2}} \, dr
\]
\[
\alpha(r) = (v + 1)((\ln \left(\frac{r}{a}\right))^2 + \ln \left(\frac{r}{a}\right)) + \frac{1}{2}
\]

\[
\beta(r) = (v + 1)^2 \left(\ln \left(\frac{r}{a}\right)\right)^2 + (1 + 2v)(1 + v) \ln \left(\frac{r}{a}\right) + v(v - 1) + 1
\]

Equation S3-1. Total integrated strain energy for the deflection of a clamped plate for the special case where only some portions of the plate have yielded.

In this paper further modifications were made to this theory in order to account for a thin layer on the top and bottom of the plate with different mechanical properties from the bulk of the plate due to surface ligand binding. The bulk can still be modelled using Equation S3-1 if \( t \), instead of being the total thickness of the plate, is just the thickness of the bulk of the plate excluding the outer layer. This equation must be modified to model the outer layer. The total strain energy of the outer layer \( U_o \) can then be added to the total strain energy of the bulk \( U_b \) to acquire the total strain energy of the plate. For calculation of \( U_o \) there are three potential scenarios where the outer layer of the plate has yielded to different extents, each requiring three different mathematical treatments.

In the first scenario, modelled by Equation S3-2, there are sections of the outer layer which have completely yielded, and some which are still fully elastic. Therefore, the yield line of the outer layer \( Z_{yo} \) intersects twice with both the outer layer-bulk boundary at \( r_1 \) and \( r_4 \) (where \( Z_{yo} = t_b/2 \)) and the edge of the plate at \( r_2 \) and \( r_3 \) (where
$Z_{yo} = t/2)$. The number of integrals needed to express the deformation energy in this scenario ends up being 7. They are as follows:
\( U_o = \pi \int_{r_1(z_\text{yo}=t_\text{b}/2)}^{r_2(z_\text{yo}=t/2)} r\alpha(r) \left( \frac{\sigma_y^3a^2(1-v^2)^2}{3E^2w_{\text{max}}} \left( \beta(r) \right)^{-\frac{3}{2}} - \frac{8w_{\text{max}}^2E}{3(1-v^2)^2a^4t_b} \right) dr 
\)

\( + \pi \int_{r_3(z_\text{yo}=t/2)}^{r_4(z_\text{yo}=t_b/2)} r\alpha(r) \left( \frac{\sigma_y^3a^2(1-v^2)^2}{3E^2w_{\text{max}}} \left( \beta(r) \right)^{-\frac{3}{2}} - \frac{8w_{\text{max}}^2E}{3(1-v^2)^2a^4t_b} \right) dr 
\)

\( + \pi \int_{r_2(z_\text{yo}=t/2)}^{r_3(z_\text{yo}=t/2)} r\alpha(r) \left( \frac{2\sigma_y^3a^2(1-v^2)^2}{3E^2w_{\text{max}}} \left( \beta(r) \right)^{-\frac{3}{2}} - \frac{2t(1-v^2)\sigma_y^2}{E} \left( \beta(r) \right)^{-1} \right) dr 
\)

\( + \frac{4t^2\sigma_yw_{\text{max}}}{3a^2} \left( \beta(r) \right)^{-\frac{1}{2}} \right) dr 
\)

\( + \frac{4\sigma_yw_{\text{max}}}{3a^3} \left( \beta(r) \right)^{-\frac{1}{2}} \right) dr 
\)

\( + \pi \int_{0}^{a} r\alpha(r) \left( \frac{2\sigma_y^2(1-v^2)}{E} \left( \beta(r) \right)^{-1} (t_b-t) \right) dr 
\)

\( + \frac{4\sigma_yw_{\text{max}}}{3a^3} \left( \beta(r) \right)^{-\frac{1}{2}} \right) dr 
\)

\( + \pi \int_{r_4(z_\text{yo}=t_b/2)}^{r_4(z_\text{yo}=t_b/2)} r\alpha(r) \left( \frac{2\sigma_y^2(1-v^2)}{E} \left( \beta(r) \right)^{-1} (t_b-t) \right) dr 
\)

\( + \frac{4\sigma_yw_{\text{max}}}{3a^3} \left( \beta(r) \right)^{-\frac{1}{2}} \right) dr 
\)
Equation S3-2. Total integrated strain energy of the shell portion of a deflected core-shell plate for the scenario where only some portions of the shell have yielded.

In the second scenario, modelled by Equation S3-3, the entire surface of the plate has yielded but not the entirety of the outer layer and so the yield line only intersects the outer layer-bulk boundary at two points, \( r_1 \) and \( r_2 \) (where \( Z_{yo} = t_b/2 \)). This requires 4 integrals to be carried out.

\[
U_{\text{total}} = \pi \int_{r_1(z_y = \frac{t_b}{2})}^{r_2(z_y = \frac{t_b}{2})} r \alpha(r) \left( \frac{\sigma_y^2 a^2 (1 - v^2)^2}{3E^2 w_{\text{max}}} \right) \left( \beta(r) \right)^{-\frac{3}{2}} - \frac{64w_{\text{max}}^2 E}{3(1 - v^2)a^4} \left( \frac{t_b}{2} \right)^3 \, dr
\]

\[
+ \pi \int_{r_1(z_y = \frac{t_b}{2})}^{r_2(z_y = \frac{t_b}{2})} r \alpha(r) \left( \frac{2\sigma_y^2 a (1 - v^2)^2}{3E^2 w_{\text{max}}} \right) \left( \beta(r) \right)^{-\frac{3}{2}} \left( \frac{2t(1 - v^2)\sigma_y^2}{E} \right) \left( \beta(r) \right)^{-1} + \frac{4t^2\sigma_y w_{\text{max}}}{3a^2} \left( \beta(r) \right)^{-\frac{1}{2}} \, dr
\]

\[
+ \pi \int_0^{r_1(z_y = \frac{t_b}{2})} r \alpha(r) \left( \frac{2\sigma_y^2 (1 - v^2)}{E} \right) \left( \beta(r) \right)^{-1} (t_b - t) \, dr
\]

\[
+ \frac{4\sigma_y w_{\text{max}}}{3a^3} \left( \beta(r) \right)^{-\frac{1}{2}} (t^2 - t_b^2) \, dr
\]

\[
+ \pi \int_{r_2(z_y = \frac{t_b}{2})}^{a} r \alpha(r) \left( \frac{2\sigma_y^2 (1 - v^2)}{E} \right) \left( \beta(r) \right)^{-1} (t_b - t) \, dr
\]

\[
+ \frac{4\sigma_y w_{\text{max}}}{3a^3} \left( \beta(r) \right)^{-\frac{1}{2}} (t^2 - t_b^2) \, dr
\]
Equation S 3-3. Total integrated strain energy of the shell portion of a deflected core-shell plate for the scenario where only the surface of the shell has yielded.

In the third scenario, modelled by Equation S3-4, the entirety of the outer layer has yielded so only one integral is needed to find $U_o$.

$$U_{\text{total}} = \pi \int_0^a r \alpha(r) \left( \frac{2\sigma_y^2 (1 - v^2)}{E} \right) \left( \frac{1}{\beta(r)} (t_b - t) + \frac{4\sigma_y w_{\text{max}}}{3a^3} \left( \frac{1}{\beta(r)} \right) \left( t^2 - t_b^2 \right) \right) dr$$

Equation S3-4. Total integrated strain energy of the shell portion of a deflected core-shell plate for the scenario where the entirety of the shell has yielded.

These integrals were carried out in MATLAB depending on which scenario the outer layer of the plate was in for a particular calculation. $U_o$ can then be added to $U_b$ to find $U_{\text{total}}$. This can then be compared to the VdW energy between the plate and the substrate, calculated in the same manner as the previous publication. The yield stress of the outer layer given a certain ligand bound to the plate surface can be determined by finding that yield stress which provides a $U_{\text{total}}$ equal to the VdW energy available for deformation given the specific experimental parameters.
New Strategies for Probing Energy Systems with \textit{in-situ} Liquid Phase Transmission Electron Microscopy\textsuperscript{4}

4.1. Abstract

Liquid-phase transmission electron microscopy (LP-TEM) is a powerful characterization tool for probing the dynamics of nanometer-scale systems in a solvated environment. When the energetic electron beam (80 – 300 kV) interacts with the solvent, radiolysis occurs, generating highly reactive species that interact with the sample. While these species are often considered harmful and great efforts are taken to mitigate their influence, many of these radiolytic products, such as hydroxyl radicals and solvated electrons, are crucially relevant to several areas of energy research. In this perspective, we propose a paradigm shift wherein solvent-derived, reactive radiolytic species generated by the electron beam are viewed as a tool for rational chemical perturbation of a material system rather than as a source of error to minimize. With an increased understanding of, and control over the chemical kinetics governing the distribution of radiolytic species, LP-TEM is poised to allow for direct imaging of chemically-driven, nanometer-scale dynamics, resulting in new insights into a range of energy-related materials.

4.2. Introduction and Background

All electron microscopes require a high vacuum environment for operation of the electron source and to minimize the scattering of electrons from species other than the sample. For TEM and scanning TEM (STEM), samples also must be thin enough to be electron transparent. As a result, these characterization methods have
historically been limited to dry, thin samples. While these techniques have been exceedingly useful for the characterization of materials at the nanoscale, an enormous fraction of all chemical and biological processes occur only in solvated environments, making them fundamentally incompatible with traditional TEM. However, with advances in microfabrication and thin film technology, hermetically sealed liquid cells have been developed to address this challenge, preventing trapped liquids from evaporating into the high-vacuum TEM environment.194 Within the last decade, LP-TEM has seen marked developments that allow for time-resolved monitoring of nanometer-scale physical and chemical events in fully solvated systems.

Most liquid cell designs, many of which are commercially available, utilize silicon nitride (SiNx) thin films as electron transparent windows to trap liquids and allow imaging of the sample. Current silicon processing methods permit the patterning of microfluidic channels, resistive heating elements, and electrodes onto the cells for in situ liquid flow, temperature-resolved, and electrochemistry experiments or any combination thereof (Figure 4-1).194-197 Alternative designs have used other materials as thin film membranes in LP-TEM cells including graphene sheets and carbon foils.198-201 Liquid cells constructed from graphene sheets offer the highest resolution possible, but also contain the smallest volume of liquid, potentially affecting results in systems that are diffusion-dependent.202-205
Figure 4-1. Liquid Phase Transmission Electron Microscopy for chemically probing energy systems. (a) Schematic showing the generation of radiolytic products via the electron beam that are then intentionally leveraged to probe specific questions about the chemistry of nanometer-scale systems. (b) Diagram of the relevant components of a TEM liquid cell holder. The sample and solvent are encapsulated in a sealed chamber capped by electron-transparent silicon nitride (SiN₃) windows. This allows for electron microscopy of fully solvated systems. Although spacer components dictate the distance between SiN₃ windows, sample chambers bulge as a result of the low-vacuum conditions in the TEM column. Microfabricated components allow for additional functionality via in situ fluid flow and heating. (c) Example of time-resolved data obtained using LP-TEM techniques. Time-lapse images show in operando electrochemical deposition and dissolution of Li at the solid-
Using these liquid cell designs, important kinetic processes can be observed directly, revealing mechanistic information about dynamics at the nanometer length scale. Most research has been focused on nanoparticle (NP) growth and etching, where beam-induced precursor reduction has allowed for real-time observation of NP formation and dissolution in both simple monometallic and more complex bimetallic systems.\textsuperscript{199, 206-211} Investigations of this sort have uncovered new kinetic growth processes in platinum and silver nanoparticle synthesis reactions.\textsuperscript{212, 213} Another emerging application of LP-TEM is the characterization of biological systems where virus particle mobility and uptake of NP therapeutic agents by cancer cells have been monitored in real-time.\textsuperscript{214, 215}

In the energy community, the primary focus of LP-TEM experiments has been in the area of battery research, where a number of important initial studies investigated the nanoscale structural consequences of lithiation and delithiation processes in the presence of real electrolytes. For example, lithium insertion onto fully submerged Si nanowire electrodes was found to occur in all crystallographic directions, leading to uniform Li shell thickness along the axial direction of the nanowire.\textsuperscript{216, 217} On the other hand, the initial lithiation events on SiNP electrodes were observed to occur asymmetrically with respect to the Si lattice.\textsuperscript{218} While these results are mechanistically important, they also impact the understanding of Li
dendrite growth, a major failure mechanism in battery technologies that can also be interrogated with LP-TEM. Dendrites are considered “dead” Li since they can no longer contact the electrode, leading to capacity fading over time. If growing dendrites become large enough to contact the cathode in a battery, potentially hazardous, internal short circuits occur. Li dendrite growth in batteries has been observed in operando, allowing for accurate quantification of growth rates using a novel contrast mechanism in LP-TEM (Figure 4-1c). The examination of battery operation in LP-TEM experiments has been used to study electrolyte decomposition in comparison with electrochemical measurements, leading to the development of systems more robust to degradation. Furthermore, LP-TEM has also been used for direct observation of the formation and dissolution of the solid electrolyte interphase (SEI); SEI formation in batteries is critical for charge transport, anode lattice protection, and cycling without capacity fade. In studies of Li-ion batteries, quantification of SEI growth kinetics has shown that interphase formation begins to occur before Li deposition, and small Li crystal deposition throughout the SEI facilitated the formation of dendrite growth. All of these results demonstrate how preliminary work using LP-TEM in the area of battery research has provided unprecedented information as well as a platform for further work.

4.3. Statement of Problem

While LP-TEM has proven itself to be a formidable tool for characterization and observation of various physical systems, the radiolytic species generated through
interactions between the electron beam and solvent have been largely regarded as a source of undesirable sample perturbation and imaging artifacts (Figure 4-1a). Radiolysis is defined as the dissociation of molecules as a result of ionizing radiation and is known to create highly reactive chemical species that are generally categorized as being either primary (arising directly from beam-solvent interactions) or secondary (arising from the reactions of primary products with each other or solvent molecules). Upon irradiation from the electron beam, individual water molecules either experience excitation or ionization (Figure 4-2a). Excitation promotes an electron from its ground-state, occupied orbital to a higher-energy, unoccupied orbital. Ionization occurs when the incident radiation has enough energy to remove electrons from the irradiated species altogether. In the case of a 200 kV electron beam interacting with an aqueous solution, free radicals (OH•, H•), gases (H₂, O₂), and redox species (e_{aq}, OH•, H•, HO₂•, H₂O₂, H⁻, OH⁻) are produced. For understanding the interactions between the radiolytic species and the sample, the products of interest are usually the hydrated electron (e_{aq}) and the hydroxyl radical (OH•). These are the most reactive components – e_{aq} being a potent reducing agent (reduction potential of -2.90 V_{SHE}) with a lifetime of t ~ 1 µs and OH• being a powerful oxidizing agent (reduction potential of +2.80 V_{SHE}) with a lifetime on the order of nanoseconds (Figure 4-2b).
Figure 4-2. Beam-driven radiolysis of water. (a) Upon irradiation by an electron beam, water undergoes a complex cascade of reactions to generate variety of energetic molecular species. Excited water and ionized water are first produced on the order of $10^{-15}$ s in what is termed the physical regime. These decompose into primary products ($\text{OH}^\bullet$, $\text{e}_{aq}^\bullet$, $\text{H}^\bullet$, $\text{H}^\bullet$, $\text{OH}^-$, $\text{H}_2$, $\text{H}_3\text{O}^+$) on the order of $10^{-12}$ s in the physico-chemical regime, which undergo further reactions with other primary products and solvent molecules to produce a steady-state of secondary products by $10^{-6}$ s in the chemical regime. (b) Standard potentials of redox-active products generated by radiolysis in a typical aqueous LP-TEM experiment.
Researchers have previously pursued a number of different strategies to mitigate the interactions between harmful radiolytic species and their samples. For example, using a microfluidic flow cell design has allowed for unreacted solvent to be continuously provided to the cell.\textsuperscript{237} However, the generation of primary radiolytic species occurs on the time scale of $10^{-12}$ s, which is considerably faster than the rate of solvent flow available in most microfluidic devices.\textsuperscript{238} Consequently, what benefits, if any, that this approach can provide are uncertain at this time. Lowering the beam dose rate to a flux on the order of $1 \text{ e}^-/\text{Å}^{2}:\text{s}$ or lower appears to be the currently preferred method for reducing sample damage.\textsuperscript{214,215,239} This strategy has become a realistic approach due to recent advances in direct electron detector technologies and compressive sensing algorithms capable of generating high resolution images from a minimum number of pixels.\textsuperscript{214,240} A less reactive, but still problematic radiolytic product is H$_2$, the production of which leads to bubble formation inside of the liquid cell.\textsuperscript{241,242} In this case, graphene may be the preferred liquid cell membrane material since it is semipermeable to H$_2$ gas under the pressure conditions found in LP-TEM.\textsuperscript{243}

Alternatively, lowering the concentration of radiolytic products can also be achieved by the introduction of a scavenger, a molecule that is sacrificially oxidized or reduced upon reaction with a radiolytic product. For example, OH$^\cdot$ is known to react with alcohols in a hydrogen abstraction reaction where the products are H$_2$O and a new radical species, the identity of which is dependent on the identity of the
alcohol scavenger.\textsuperscript{230} For instance, in an \textit{in situ} AgPd galvanic replacement reaction, isopropanol has been used to scavenge OH\textsuperscript{*} to create net reducing conditions:

\[
\text{OH}^* + \text{CH}_3\text{CHOCH}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{C}^*\text{OHCH}_3
\]

where CH\textsubscript{3}C\textsuperscript{*}OHCH\textsubscript{3} is a strong reducing agent (\(-1.8 \text{ V}_\text{SHE}\)).\textsuperscript{244} This effectively converts the oxidizing OH\textsuperscript{*} to a highly-reducing species which, coupled with the presence of \(e_{\text{aq}}^-\), shifts the chemical environment to one that is net reducing. Aside from alcohols, graphene has been shown to decrease the amount of sample damage incurred the electron beam. One explanation for this observation is that the high conductivity of graphene may prevent electrostatic charging effects through charge extraction and/or delocalization.\textsuperscript{245, 246} However, it has also been shown that graphene, graphene oxide, and graphene quantum dots can act as effective OH\textsuperscript{*} scavengers.\textsuperscript{247-250} The proposed mechanisms for this include electrophilic addition of OH\textsuperscript{*} to \(\pi\) bonds and further oxidation of functional groups on the graphene nanostructures.\textsuperscript{247-249} This chemistry has been specifically applied to LP-TEM experiments where the addition of graphene nanostructures to solutions of beam-sensitive, DNA-based materials in a traditional SiN\textsubscript{x} liquid cell resulted in significant sample protection.\textsuperscript{227} Aside from these few examples, it is worth noting that there are many other known scavengers for the products of water radiolysis that have yet to be applied to a LP-TEM context.\textsuperscript{251}
4.4. Perspective: Tailoring Radiolysis for the Generation of Desired Reactive Species

Despite efforts to generate pristine imaging conditions in LP-TEM experiments, the goal of completely removing the influence of radiolytic species is unrealistic given current imaging and detector technologies. Here, we propose a subtle but important shift in emphasis regarding this issue: rather than viewing the products of the electron beam as a problem to address, consider the highly reactive radiolytic species as a stimulus source that can be leveraged to better understand a particular physical system (Figure 4-1a). This approach is particularly appealing for the basic energy sciences community, where researchers routinely interrogate systems that require similar reactive species, e.g. in battery applications, water remediation, photoelectrochemical water splitting, and solar energy.\textsuperscript{235, 252-257} We view this approach as having the potential to cause a paradigm shift similar to the realization in traditional electron microscopy that, in addition to being used for imaging, the beam can serve as a powerful tool for spectroscopy, providing compositional and electronic structure information about nanometer-scale samples. However, in order for this to be realized, the beam driven radiolysis of various solvents needs to be understood beyond the generation of net-reducing or net-oxidizing environments. With a more detailed knowledge of and control over the mechanisms at play, the environment of the liquid cell may be tailored to probe specific, energy-related phenomena in a rationally-designed, empirically-informative
manner. Here, we will highlight three potential approaches towards the goal of a tailored liquid cell environment that have yet to be broadly applied to LP-TEM experiments.

4.4.1. Engineering the Lifetime of Free Radicals

Some of the exceedingly reactive species produced by radiolysis are radicals, molecules containing a singly occupied orbital. Radicals are generated when a weak bond in an electronically excited molecule can undergo a homolytic cleavage, where each molecular fragment is left with one of the once-shared electrons. This removes a valence electron from an orbital where it was paired (Figure 4-3a). Being a result of electron removal, free radicals are an inherently electron deficient species, and can be stabilized by inductive effects of neighboring substituents and delocalization by resonance (Figure 4-3b-c). Conversely, radicals are destabilized when created on increasingly electronegative substituents. For example, the creation of a radical on a highly electronegative heteroatom, such as fluorine, will be destabilizing relative to the same process on a less electronegative atom. This points to the possibility of chemically designing the system so that particular radical species will be destabilized, making them more likely to recombine (i.e. have a shorter lifetime) than interact with the sample. On the other hand, specific radicals can be intentionally stabilized if the interaction with the sample is desirable for probing an energy-related chemical process. The most straightforward way to apply this principle is by way of solvent choice. If radical species are undesirable for the sample being probed in LP-TEM, a
halogenated solvent is ideal (e.g. chloroform or tetrachloroethylene). Conversely, if a radical species is necessary to create desired chemical conditions, an aromatic solvent is preferred (e.g. benzene or toluene). These chemical principles may be applied to the addition of scavenger species to similarly influence radical lifetimes.

![Figure 4-3](image)

**Figure 4-3.** Radical generation and the chemical principles of stabilization. Upon excitation from the electron beam, (a) weak bonds undergo a homolytic cleavage to generate radical species that may be stabilized by (b) increasing substitution of groups that donate electron density, denoted with blue arrows from methyl substituents, and (c) delocalization as a result of resonance, where the electron density of the radical is shared across multiple atoms in the structure.
4.4.2. Engineering the Lifetime of Solvated Electrons

The second inevitable radiolytic product responsible for significant sample perturbation is the solvated electron, \( e_s \) (e\(_{aq}^-\) in water). This species is generated when an electron is liberated via a beam-driven ionization event and remains in the solvent. Immediately following the liberation event, the solvent is not yet polarized in response to the presence of the additional charge density presented by the \( e^- \). Under these conditions, the electron is considered “dry” and is highly unstable, making it likely to annihilate by recombination with the surrounding solvent molecules. However, if solvent molecules are able to reorient and/or polarize in response to the presence of the \( e^- \), a potential well is created that stabilizes the species. This electron is considered “solvated” and will experience a considerably longer lifetime compared to the “dry” state, making it more likely to react with other solute species.

In determining whether a solvent stabilizes or destabilizes \( e_s^- \), both thermodynamic and kinetic parameters are important to consider (Figure 4-4). The ability for the solvent to polarize and coordinate the \( e_s^- \) is largely responsible for the depth of the thermodynamic potential well in which the \( e_s^- \) resides and is governed by the dielectric constant of the solvent. A high dielectric constant solvent will more easily polarize and thermodynamically stabilize the \( e_s^- \) compared to one with a low dielectric constant. Although it is tempting to consider the depth of the potential well to be the dominant parameter in dictating \( e_s^- \) stability, the system is often more strongly governed by kinetic factors. In order to coordinate a dry electron, the solvent
must reorganize, often at the expense of breaking of multiple attractive intermolecular solvent-solvent interactions. This imposes an energetic barrier that must be traversed in order for the electron to become solvated and stabilized. If the reorganization energy is too high, the electron will remain kinetically trapped in the dry and more reactive state. Intuitively, the same high-dielectric constant solvents capable of thermodynamically coordinating the $e_\text{s}^-$ will also tend to have favorable intermolecular interactions and thus high reorganization energies. Therefore, highly polarizable solvents tend to support kinetically-trapped, short-lived $e_\text{s}^-$ that annihilate before interacting with the sample, while more non-polar solvents tend to have lower reorganization energy barriers, facilitating longer-lived, solvated $e_\text{s}^-$ that are more reactive to the sample.

Figure 4-4. Reaction diagrams of beam-liberated electrons in two limiting cases. After a liberation event, an electron is “dry”. Solvent molecules must break intermolecular bonds to overcome a reorganization energy barrier, $E_{\text{R},\text{R}}$. 

kinetically stable, self-annihilating, less reactive to sample, $\tau$ short

thermodynamically stable, stabilized by solvent shell, more reactive to sample, $\tau$ long
to polarize around and solvate the electron. Once solvated, the electron is thermodynamically stabilized by the depth of the solvation energy well, $E_s$. For (a) high-dielectric solvents, intermolecular bonds are favorable, $E_R$ is large, and the electron remains kinetically trapped. For (b) low-dielectric solvents, intermolecular bonds are weak, the $E_R$ barrier can be overcome by thermal fluctuations, and the electron is more thermodynamically stabilized. In the latter case, the electron will be longer-lived and more reactive to the sample compared to the former case.

Numerous empirical observations from the radiolysis literature support this model of electron solvation. For example, water, which has a high dielectric constant due to its permanent dipole moment, is capable of strong coordination of the $e_\mathcal{s}$, resulting in a deep thermodynamic potential well. However, the energy barrier associated with the breaking of numerous H-bonds in water results in a high reorganization energy. Additionally, the solvation sphere formed around $e_\mathcal{s}$ must be large to accommodate the significant charge distribution; for $e_{aq}$ this is estimated to be 2.5-3.0 Å and serves to further increase the energetic cost of solvent reorganization.\textsuperscript{258} These factors make solvation kinetically difficult, trapping the electron in a dry state associated with a short lifetime ($\sim$ µs).\textsuperscript{232} Conversely, solvents with a smaller dielectric constant and a lower barrier to reorganization, e.g. hexamethylphosphoramide, have been observed to support $e_\mathcal{s}$ lifetimes as long as several hours.\textsuperscript{259} In general, the lifetime of $e_\mathcal{s}$ is known to decrease with increasing solvent dielectric constant: ammonia > amines > alcohols > water. However, it should be noted that there are exceptions to this trend. Although tetrahydrofuran (THF) is less polar than many of the aforementioned solvents, the annihilation of $e_\mathcal{s}$ occurs
quickly with a reaction rate \( \sim 10^{-11} \text{ to } 10^{-12} \text{ M}^{-1}\text{s}^{-1} \). While there is limited empirical data for \( e_\cdot \) lifetimes in specific solvents, the general chemical principles outlined above can be used to tailor the relative stability of \( e_\cdot \): For solvents with a high dielectric constant (e.g., water, dimethylsulfoxide, or ethanol), the electron is likely to be kinetically trapped and unstable, resulting in annihilation with the surrounding solvent and a decreased reactivity towards the sample. For solvents with a low dielectric constant (hexane, toluene, benzene), the electron is likely to be thermodynamically stabilized via solvation, resulting in a long lifetime and an increased likelihood for reaction with the sample.

### 4.4.3. Regulating Radiolytic Products via Beam Dose

It is well known that lowering the radiation dose associated with the electron beam during an imaging experiment mitigates the effects of radiolytic products. Much of the data on this strategy comes from the cryo-TEM community, where biological samples are frozen to preserve native structure and decrease the ability for radical species to diffuse throughout the sample.\(^ {261-265} \) The beam dose in a typical cryo-TEM experiment can be as low as \( 0.2 \text{ e}^-/\text{Å}^2 \) while locating the sample and focusing, with a cumulative dose to collect a high-resolution image of \( 10-30 \text{ e}^-/\text{Å}^2 \), depending on the accelerating voltage (\( 100 \text{ – } 300 \text{ keV} \)).\(^ {266, 267} \) For comparison, beam conditions for collecting a standard bright field image of an inorganic sample at 200 keV can be 1500 \( \text{e}^-/\text{Å}^2 \) or higher.
The principle of lowering beam dose to lower radiolysis yield has been employed by several in the LP-TEM community with reports of improved imaging conditions and mitigated sample damage.\textsuperscript{214, 215, 239} While this general observation is straightforward, translating quantitative conclusions from cryo-TEM experiments to those in the liquid phase can be challenging since the sample environments differ wildly. Ross and coworkers have recently conducted simulations aimed at predicting the distribution of radiolytic species as a function of beam dose in liquids relevant to LP-TEM (Figure 4-5).\textsuperscript{226} Although these results demonstrate that for pure, deaerated water, the concentration of radiolytic products indeed decreases with lowered beam dose, the presence of even small quantities of dissolved gasses significantly changes the relative distribution of radiolytic species. Therefore, in realistic systems that are certain to contain a variety of ions, gases, and the sample of interest, it is likely that the ratio of different radiolytic products will be highly dose-dependent. It should be noted that these data are only relevant for water, highlighting the need to conduct similar investigations into beam dose effects in other solvents. As a general rule, lowering beam dose will decrease the absolute concentration of radiolytic species, but caution is warranted in drawing conclusions about the relative concentration under similar conditions. With a greater understanding of the chemistry of radiolysis, we foresee beam dose also being a powerful tool for controlling the chemical environment in LP-TEM experiments.
Figure 4-5. Simulations of radiolytic product concentrations as a function of radiation dose. Ross and coworkers found that for (a) neat, deaerated water, the distribution of radiolytic products is constant and increases proportionally with beam dose. For (b) aerated water, the distribution of radiolytic products differs greatly with beam dose. The unit Gy/s represents the joules of energy applied per kilogram of liquid as a function of time.

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The field of radiation chemistry has provided key mechanistic insights into the production of reactive species via radiation. However, it should be noted that the radiation conditions used in many of these studies do not represent the conditions present in a TEM-based liquid cell experiment. Traditional ionizing radiation experiments employ a dose $\leq$10 Gy/s and pulse radiolysis experiments, in which transient species are monitored spectroscopically after short exposure to an electron beam, deliver a single dose on the order of $\sim$10 Gy/ns or $\sim$10 Gy/µs. For comparison, the continuous dose rate associated with a 200 keV electron beam interacting with water is on the order of $10^7$ Gy/s. This makes direct and quantitative comparison to results in the extensive radiation chemistry literature
challenging at best. For example, the ability to use pH to control the yield of secondary radiolytic products is implicated in numerous reports in the literature and would be significant in controlling conditions for LP-TEM experiments.\textsuperscript{270,271} Fielden and Hart reported that at pH=2, virtually all $e_{aq}^-$ can be converted to H\textsuperscript{*} and that at pH=13, H\textsuperscript{*} can be completely converted to $e_{aq}^-$. Unfortunately, the dose associated with these processes was 0.5 Gy/s (administered by 300 pulses of radiation at 10 pulses/s) and it was noted that higher radiation doses would interrupt these reactions by radical-radical interactions.\textsuperscript{270} While pH and other factors will unequivocally alter the distribution of radiolytic products, a resurgence in the field of radiation chemistry as it pertains to the high-dose regime will be necessary to rationally control beam-induced chemistry. Nonetheless, general principles and certain qualitative trends still apply and can act as a starting point for developing better chemical intuition about the environment in a LP-TEM experiment.

4.5. Future Directions and Opportunities

4.5.1. Selecting Novel Solvents Relevant to Energy Research Systems

Given the importance of different solvents in controlling radiolytic species, a relatively unexplored but exciting direction may be in the use of unconventional solvent systems such as ionic liquids (ILs). These have previously been used in LP-TEM without the use of a hermetically sealed sample cell because of their low vapor pressure but have not been explored specifically as radiolytically-tunable
matrices. Several preliminary examples in the literature have shown that the use of ILs in lieu of more traditional solvents has resulted in a decrease in anomalous beam effects compared to the corresponding aqueous solvents. Radiation studies with ILs have shown several different species including \( e^- \) and various radicals, depending on the structure of the IL organic cation. Imidazolium-based ILs readily form radicals that are stabilized by delocalization in the imidazole ring substituent, whereas non-heterocyclic ammonium-based ILs have not shown radicals of the same stability (Figure 4-6a). This would make imidazolium-based ILs ideal for experiments where sample perturbation by radical species is desired, e.g. in monitoring degradation of a catalyst by oxidation. Conversely, if radical species are undesirable, an ammonium-based IL should be used. Similarly, solvated electrons are produced in ILs with largely differing reactivity depending on cation structure. In the case of imidazolium- and pyridinium-based ILs, it has been observed that \( e^- \) are rapidly scavenged by the solvent cations and unable to react with species contained within the liquid. However, \( e^- \) produced in ammonium-based ILs tend to be longer-lived and readily react with the sample (Figure 4-6a). While ammonium-based ILs generally have higher dielectric constants than imidazolium- and pyridinium-based systems, ILs are not subject to the same kind of intermolecular interactions as conventional solvents. As a result, the trends established previously regarding reorganization energy barriers and solvation wells are not necessarily applicable to ILs. Indeed, initial radiation experiments with ILs suggest that specific classes may be capable of generating a larger disparity in the population of radicals compared to \( e^- \).
than more traditional solvent systems.\textsuperscript{275-278} This highlights an exciting opportunity for IL-based solvents to act as a more tailorable alternative for controlling the chemical environment in energy-related LP-TEM experiments.

4.5.2. Strategies for Further Battery Improvement and Development

Decreases in battery performance over time are commonly attributed to changes at the electrode/electrolyte interface facilitated by decomposition of the electrolyte at the high reduction potentials necessary to operate the anode in a Li-ion battery.\textsuperscript{280-282} Although during initial cycling of the battery these crucial processes form the protective SEI layer, if electrolyte degradation continues over time, the SEI can grow and change in morphology and composition, leading to capacity fading and safety hazards.\textsuperscript{283-288} Since the electrochemical decomposition of the electrolyte can be mimicked by high-energy electron transfer reactions,\textsuperscript{222} solvated electrons generated by LP-TEM are ideal for characterizing SEI formation as a consequences of electrolyte reduction. Observing the kinetics of these processes at the nanometer scale will be of particular significance when characterizing the performance of next-generation electrolytes for batteries based on Li and other alternative metals.\textsuperscript{252, 289}

Another area of battery-related research where radiolytic product tailoring may be particularly useful is in the development and understanding of electrolyte additives. The incorporation of additives to a pre-existing electrolyte is a simple strategy that has been shown to improve battery performance by assisting the formation of the SEI, often through a radical-anion mediated reaction (Figure
4-6b). For example, a radical anion formed on ethylene carbonate has been shown to react with other electrolyte components, leading to extremely insoluble products that form a more stable, compact SEI. A similar example is the development of prop-1-ene-1,3-sultone (PES), which was shown to be an effective additive by forming a stable radical anion that formed high amounts of reduced, insoluble SEI components. For comparison, a radical anion of lower stability was generated on propane sultone that showed decreased reducing ability and the formation of a less protective SEI. These results highlight an opportunity to rationally tailor the lifetime of various radical species and directly observe the real-time, in operando consequences on SEI formation using LP-TEM for the development of next-generation battery electrolyte additives.

4.5.3. Interrogating Instabilities in (Photo)Catalytic and Photoelectrochemical Systems

In many (photo)catalytic and photoelectrochemical reactions, species such as OH• and other oxide radicals, are known to be mechanistically significant. Specific areas where this applies are artificial photosynthesis and systems in which inorganic oxide catalysts mediate photoelectrochemical reactions such as water splitting and water remediation. These cases are known to suffer from structural instability and deterioration due to the presence of radical species (Figure 4-6c). In “artificial leaf” designs, biological photosynthetic proteins are used that experience degradation via reactive oxygen species (ROS) generated as a natural by-
product of charge separation and multielectron redox reactions. LP-TEM experiments could be employed to systematically introduce beam-generated ROS, such as OH•, and capture the nanoscale mechanisms of degradation or, in the case of added molecular antioxidants, protection (Figure 4-6c). For photoelectrochemical and catalytic reactions involving inorganic oxide structures, the mechanisms of chemically-mediated instability and degradation are poorly understood. Introduction and stabilization of specific radical species while monitoring dynamic changes in structure would be a powerful tool in elucidating mechanisms underlying this process. The ability to make and test chemical hypotheses regarding nanometer-scale structure and kinetics will be crucial for creating next-generation photocatalytic and photoelectrochemical systems for energy storage and production.
Figure 4-6. Future directions and experiments enabled by LP-TEM. (a) Ionic liquid solvent components capable of strongly stabilizing radiolytic products such as radicals and solvated electrons; these may be better able probe a variety of nanoscale chemical processes than conventional solvents. (b) Proposed investigation of electrolyte-mediated SEI formation in the presence (bottom) and absence (top) of radical-stabilized additives. (c) Proposed investigation of the decomposition of photoelectrochemical catalysts via electron-beam generated radiolytic species in the presence (bottom) and absence (top) of antioxidant scavengers.
4.6. Conclusion

In LP-TEM experiments, the interaction of the electron beam with the solvent can be thought of as a nanometer-scale source for deliberately introducing specific chemistry to a system of interest. Rather than developing complex methods for delivering foreign material or energy and observing the consequences, the beam can trigger a perturbation directly and in a manner that is chemically-relevant for a variety of energy-related process. This represents a significant shift in perspective and is one that requires an understanding of the chemical principles governing radiolysis and the stability of highly-energetic molecular species. The concepts of radical stability, solvated electron thermodynamics, and dose-dependent radiolytic chemistry are crucial elements for enabling a more tailored environment in LP-TEM experiments. By highlighting these ideas and proposing novel experiments that leverage radiolytic species, we hope to spur the field in this new direction. The opportunities for new mechanistic understanding are profound and far-reaching. The energy community is poised to take advantage of LP-TEM to advance fundamental knowledge and enable next-generation technologies in battery systems, electrochemistry, photocatalysis and beyond.
4.7. Funding Acknowledgement

This work was supported by the Robert A. Welch foundation through a young investigator award. S.M.R. wishes to acknowledge financial support from a National Science Foundation Graduate Research Fellowship #1450681.
Chapter 5

Conclusions and Future Outlook

Overall, this thesis explored the deformation of highly compliant metal nanostructures. Chapter 2 discussed the development of the experimental model used, where extremely-thin colloidal silver nanoplates are grown via a seeded method.\textsuperscript{150,151} We then leveraged conventionally weak van der Waals interactions to deform the nanoplates over a small spherical template particle resting on a flat surface, transforming a flat geometry to a curvilinear one. The result of this process was plastic deformation in the nanoplate, confirmed by analytical modelling (modified Kirchhoff-Love plate theory), finite element simulations, and high-resolution TEM imaging. The local deformation of the nanoplate around the template sphere also generated unique, flower-shaped bend contours in routine TEM characterization that corresponded to crystallographic tilting of a (220) family of planes. It was also determined that based on the proximity of two templates near one another, different and more complex curvilinear geometries could be generated. In this way, the singular-templated deformation could be viewed as a singular canonical structure upon which a vast array of additional architectures can be built that would
otherwise be enormously challenging to fabricate via other methods. This work introduced a new method for the post-synthetic shape control of nanoparticles, one that challenges the conventional notion of nanoparticles as static, unchangeable structures. We anticipate that deformed nanoparticles such as this might have unprecedented catalytic and optical activity, making them an interesting subject for future studies in nanoparticle-driven catalysis and plasmonics.\textsuperscript{169-171}

Chapter 3 utilized the previously developed experimental model\textsuperscript{187} to explore the nanoscale effects of ligand chemistry. The result of this work was the discovery and characterization of a fundamentally new, size-dependent nanoscale coupling between chemistry and mechanics. It was observed that ligand bond strength was directly related to the mechanical strength of the silver nanoplates, as characterized by our high-throughput method of measuring bend contours of deformed plates. It was determined that the system could be modelled from a continuum-mechanics perspective by viewing the nanoplate as a core-shell structure in which the shell corresponded to a few atomic layers at the metal surface with a higher yield stress. This modelling could also be related to observed lattice expansions and contractions, meaning that the behavior of the system could also be understood in terms of atomic-scale occurrences. This multiscale characterization of the nanoscale coupling between ligand binding strength and mechanical strength demonstrates that sub-microscale molecular events can lead to global changes in the behavior of a nanoparticle. Most inorganic nanoparticles and microscale systems all involve
interfacial interactions with organic molecules, meaning that this effect has increased our fundamental understanding of and has serious implication for such systems.

In combination, these works provide a framework for using compliant metal nanostructures as a basis for dynamic systems, capable of restructuring as well as displaying differential behavior, actuated by ubiquitous forces and chemistry.

Chapter 4 explores the technique of liquid-phase TEM as an extremely powerful tool for characterizing nanostructures. Radiolytic products generated by interactions of the beam with sample liquid, are generally known to damage samples and interfere with experiments. However, we suggest that these reactive species can be used as a tool for sample perturbation, and present design rules based on fundamental chemical principles as well as classic radiation studies to potentially tailor the production and distribution of radiolytic species. The understanding and innovation where characterization tools and techniques are concerned aids in the characterization of new nanoscale systems, such as the ones presented in this work.
Appendix – Controllably Hollow AgAu Nanoparticles via Non-Aqueous, Reduction Agent Assisted Galvanic Replacement

1. Abstract

The galvanic replacement reaction is a robust tool for the controlled synthesis of hollow and semi-hollow bimetallic nanostructures, which have applications in a range of science, engineering, and medical fields due to the tunability of their localized surface plasmon resonances (LSPRs) and surface chemistry. Here, we describe a controllable galvanic replacement of Ag by Au coupled with co-reduction, performed in non-aqueous solvents including methanol, ethanol, and a N,N-dimethylformamide:toluene mixture and yielding hollow and semi-hollow alloyed nanoparticles. Structural control, from semi-hollow to nanoshell, and plasmon tunability is demonstrated via control of the Au:Ag stoichiometry. We show the high structural dependence on temperature, with striking changes in nanoparticle surface smoothness and pinhole density, and reveal the optimal reaction temperature to be 65°C in alcohols. Through optimizing this reaction, we obtained smooth closed shell

AgAu alloy nanoparticles with LSPRs tunable from 494 nm to 567 nm. This work provides a framework for galvanic replacement of large anisotropic Ag nanoparticles with Au in non-aqueous media, which can be extended to other solvent systems suitable for air-sensitive metals and precursors.

2. Introduction

Nanoparticles (NPs) of free-electron metals such as Ag, Au, and Al have found applications across the biological and chemical sciences because they strongly interact with light through a phenomenon called localized surface plasmon resonance (LSPR).\textsuperscript{180} LSPRs are a light-driven, collective oscillation of conduction electrons in a metal NP. Their excitation leads to wavelength-dependent photon absorption, photon scattering, and a large enhancement of the local electric field. These effects can be harnessed for use in, for instance, surface enhanced spectroscopies such as surface enhanced Raman spectroscopy (SERS)\textsuperscript{294} and surface enhanced fluorescence,\textsuperscript{295} as well as in biological sensing, catalysis, and photodetection.\textsuperscript{296-301}

Using LSPR properties in sensing and spectroscopy, for instance, requires tuning of the plasmon wavelength, scattering/absorption ratio, and near-field enhancement, such that it can be applied to a wide array of chemical systems. This tailoring can be achieved by manipulating the NP’s size, composition, and shape.\textsuperscript{180, 302, 303} Amongst common shapes, hollow NPs are of particular interest due to the additional degree of freedom afforded by the shell thickness, providing further tunability of the LSPR energy across the visible and NIR, for Ag and Au, as well as
opportunities to augment near-field enhancement due to plasmon hybridization between the shell and void.\textsuperscript{169, 304} Nanoshells and other hollow architectures can indeed perform better in applications such as SERS,\textsuperscript{305} imaging, and photothermal therapy.\textsuperscript{306} Furthermore, hollow NPs are of interest owing to their high surface area to mass ratio, their ability to carry a cargo,\textsuperscript{307} and their potential to enable studies of chemical reactions in nanoscale volumes.\textsuperscript{308}

Hollow NPs can be synthesized by various methods including etching of the core in core-shell particles, the nanoscale Kirkendall effect, and by nanoscale galvanic replacement.\textsuperscript{309-313} The galvanic replacement reaction is a particularly robust and adaptable method for creating hollow NPs. Simply put, it is a spontaneous replacement reaction between the atoms of a sacrificial NP template by metal ions with a lower reduction potential \textit{i.e.} of a more noble metal.\textsuperscript{310} The template metal is thus oxidized while the more noble metal ions are reduced on its surface, resulting in a replacement; this process occurs on the template surface at areas of high energy, creating surface pinholes.\textsuperscript{312} Continued replacement at the pinholes results in a gradual hollowing of the NP.\textsuperscript{313} The shape of the resulting structure is directed by the template's, allowing for exquisite control in the case of metals such as Ag and making this route particularly attractive for controlled syntheses.

A well-known galvanic replacement reaction is that of Ag by Au, where the stoichiometric ratio between the Au ions (typically Au\textsuperscript{3+}) and Ag template atoms is 1:3 (0.33Au:Ag). Alloying readily occurs between Ag and Au, owing their nearly matching lattice constants and excellent miscibility.\textsuperscript{314} As the reaction proceeds, the
alloyed structures, containing two plasmonic metals, progress from semi-hollow to hollow and porous NPs.\textsuperscript{310, 312, 315} Further galvanic replacement removes Ag by a dealloying process, generating hollow Au nanocages.\textsuperscript{316} Dealloying can be overcome by adding a reducing agent to the reaction (a process called co-reduction), leading to alloy structures even for stoichiometries larger than 0.33Au:Ag.\textsuperscript{308} This approach also often reduces the roughness and occurrence of pinholes if the co-reduction step is slow; such structures can be completely pinhole-free and liquid-filled, enabling aqueous, electron-beam driven electrochemical reactions, for instance.\textsuperscript{308}

Galvanic replacement reactions involving Ag and Au are usually performed in aqueous media.\textsuperscript{310, 317, 318} Of the few reducing agent-assisted reactions, to the best of our knowledge, all have been performed in aqueous media: one for Pd and Pt,\textsuperscript{319} and two other, for Ag and Au,\textsuperscript{308, 320} with only one work reporting closed NP structures.\textsuperscript{308} Replacement in aqueous media limits the synthesis, functionalization, and application of NPs: non-aqueous syntheses could, for instance, allow for the encapsulation of water-insoluble molecules inside the NP cavity, as well as enable the galvanic replacement of, or with, metals unstable in water. Furthermore, the ability to perform non-aqueous galvanic replacement of Ag NP templates of various sizes and shapes, with control over the stoichiometry of the final product, has important implications for LSPR tuning and surface functionalization. Reports of non-aqueous galvanic replacement approaches, which exist only for toluene, dichlorobenzene, and chloroform, all focus on the replacement of sub-25 nm isotropic Ag templates with Au
to produce Au nanocages;\textsuperscript{321-326} as of yet none involve large, anisotropic structures or tunable morphologies.

Here, we present a new method for the galvanic replacement of large, anisotropic Ag NPs in methanol, ethanol, and a N,N-dimethylformamide (DMF):toluene 1:1 mixture. Large (>50 nm) plasmonic NPs synthesized in aqueous media were transferred with additional capping agent in the non-aqueous solvents, enabling the use of established synthetic protocols for size and shape control. The products of the galvanic replacement in these solvents can be manipulated by temperature, Au:Ag stoichiometry, and the presence of a reducing agent (enabling co-reduction). While differences in final NP morphology from each solvent are observed, including pinhole occurrence and shell smoothness, the two alcohol solvents respond in an analogous fashion to changes in reaction parameters, including stoichiometry and temperature. This work provides a new platform for the synthesis of a wide array of metallic NPs in water-free conditions that are readily adaptable to air-free systems for the manipulation of highly reactive elements.

3. Results and Discussion

3.1 Galvanic Replacement if Ag NPs in Alcohols

Ag NPs composed of 85% isotropic NPs and 15% nanorods (Figures A1 and SA1) were synthesized by a seeded growth method and dispersed in either methanol,
ethanol, or 1:1 DMF:toluene solvent mixture with a polyvinylpyrrolidone (PVP) capping agent. Addition of 0.2Au:Ag from HAuCl₄ (a Au³⁺ precursor) and of a co-reduction agent (ascorbic acid) to these non-aqueous solutions created semi-hollow alloyed nanostructures (Figure A1). All observed NPs underwent replacement, suggesting that the addition of cationic Au leads to NP hollowing regardless of the presence of crystallographic twins and defects; this replacement also occurred whether the nanoparticles were isotropic (sphere-like) or anisotropic (rod-shaped). The resulting alloyed NPs' void contains a non-aqueous solution. Transmission electron micrographs (TEM) display points of light contrast in the shell of some of the NPs, indicative of the presence of pinholes.
Figure A1. Overall reaction, precursors, and optimized smooth, semi-hollow AgAu NPs synthesized in non-aqueous solvents with 0.2Au:Ag. a) Schematic and overall chemical equation of the galvanic replacement reaction of a Ag NP template with cationic Au, b) TEM images of the synthesized Ag precursor, and semi-hollow galvanic replacement products obtained in c) methanol (MeOH) at 65°C, d) ethanol (EtOH) at 65°C, and e) 1:1 DMF:toluene at room temperature.

In both alcohols, the product NPs show partial replacement; the co-reduction agent is effective at preventing dealloying and loss of structural integrity. For the reactions performed with 0.2Au:Ag, we obtained the expected\textsuperscript{316} hollow nanocage in the absence of ascorbic acid (Figure SA2). When present, ascorbic acid slowly reduces the removed Ag\textsuperscript{+} as well as a portion of the added Au\textsuperscript{3+} onto the particle surface during
replacement such that instead of hollow nanocages, NPs synthesized at 65°C with a reducing agent have a closed, smooth surface with solvent trapped inside the void of the particle (Figure A1). At higher Au:Ag ratio, such as 0.5Au:Ag, the co-reduction agent prevents the NPs from dealloying to small fragments (Figure S5-2). Co-reduction therefore offers the opportunity to achieve a broader range of compositions and morphologies from galvanic replacement approaches in non-aqueous solvents.

The ascorbic acid-assisted galvanic replacement of Ag by Au in methanol, ethanol, and DMF:toluene all result in semi-hollow to hollow NPs, with smooth continuous shells for the alcohols. However some differences are observed and are important to the implementation of galvanic replacement in non-aqueous solvents. First, the NP’s surface roughness is higher in ethanol than in methanol for equivalent reaction conditions (Figure A1 c and d); a related observation is that the ethanol-produced NPs also exhibit more pinholes. Second, the reaction rate in ethanol is consistently slower than in methanol. For instance, at 65°C and with 0.5Au:Ag, the initial solution color change in response to the addition of Au occurred in a few seconds in methanol and a few minutes in ethanol. This first step represents the initial, fast galvanic replacement as observed in aqueous systems. Slower co-reduction then progresses until the dispersed NPs attain the vibrant colors in Figures A2 and A3, reaching near-completion after 30 minutes in methanol, and an hour in ethanol. The morphology differences observed between the two solvents are likely related to the difference in relative rates of initial galvanic replacement and
continuous co-reduction. The initial galvanic replacement is much slower in ethanol than methanol (minutes versus seconds). Then, the subsequent co-reduction is also slower in ethanol than in methanol (and hour versus half an hour), although their rates are more similar than the initial galvanic replacement rates. The ratio of co-reduction completion time to initial replacement substantial completion time is lower in ethanol (co-reduction is relatively fast). Smooth NPs are thus produced when the co-reduction step is slow compared to the initial replacement step, because it allows for a slow restructuring of the NP surface. This leads to rougher particles in ethanol, unlike what has been reported for PdPt nanocubes upon manipulation of the co-reduction; for PdPt, fast galvanic replacement coupled with slow reduction led to rough, irregular NPs.\textsuperscript{319}

The currently observed NP morphology’s relationship to reaction rate is further confirmed by galvanic replacement performed in DMF:toluene at room temperature, which also has a low ratio of co-reduction completion time to initial replacement substantial completion time (similar to ethanol’s) and rough surfaces (Figures A1e, SA3, and SA4). In this non-aqueous solvent, the initial replacement is comparable to ethanol’s (several minutes), and then the co-reduction slowly progresses over two hours. The resulting nanostructures are rougher than NPs synthesized in methanol, supporting the importance of the relative speed of co-reduction and initial replacement, where a relatively slow initial replacement yields smoother particles. The solvent identity therefore affects the reaction rate and the
final morphology of the product. Such differences can be attributed to solvent-specific
diffusion rates, dielectric constants, as well as metal ion speciation.328-330

3.2 Structure and Plasmon Tuning via Stoichiometry Control

Galvanic replacement in alcohols offers a simple route to manipulate the NPs’
structures and optical properties through the control of the ratio of template (Ag) to
ion (Au) atoms. The colloidal samples (Figure A2a) synthesized at 65°C exhibit a
striking color change as more Au is added, from orange for 0.2Au:Ag to pink for
0.3Au:Ag to violet for 0.5Au:Ag in both methanol and ethanol. In DMF:toluene, the
solutions obtained are orange and blue at 0.2Au:Ag and 0.5Au:Ag, respectively
(Figure SA5). The solutions’ vibrant colors are in sharp contrast with the dull, grey-
ish solutions created from ascorbic acid-free galvanic replacement (Figure SA2).
Changing the Au:Ag ratio from 0.2 to 0.5 results in a LSPR shift from 494 nm to 567
nm, from UV-Vis extinction spectroscopy (Figure A2f). This redshift can be attributed
to the increased concentration of Au in the alloy331 as well as the increasing size of
the void.170 The morphology of the sample (Figure A2 b to e) indeed evolves from
semi-hollow NPs (0.2Au:Ag) to nanoshells (0.5Au:Ag); regardless of the Au:Ag ratio,
the resulting NPs are always smooth, closed structures with little appearance of
pinholes.
Figure A2. Concentration effects on the morphology and LSPR for the ascorbic-acid assisted replacement of Ag by Au at 65°C in methanol. a) NPs obtained from galvanic replacement of Ag by Au in methanol, from 0.2Au:Ag (left) to 0.5Au:Ag (right), b-e) corresponding TEM images, and f) normalized extinction spectra. Additional images in Figures SA6 to SA9.

A similar concentration dependence is observed for reactions performed in ethanol (Figure A3). The NP suspensions have vibrant colors, and exhibit the same morphology and composition development with increasing Au:Ag. TEM images (A3b to e) confirm that the void size increases to create nanoshells as the ratio reaches
0.5Au:Ag. However, the surface roughness and occurrence of pinholes in the replaced NPs appears higher in ethanol, regardless of temperature, due to the difference in relative rates of initial galvanic replacement and co-reduction. Finally, the concentration dependence of the final void size appears to be equivalent in ethanol and methanol, with semi-hollow structures observed with low Au:Ag ratio, and fully hollow shells for higher Au:Ag ratios.
Figure A3. Concentration effects on the morphology and LSPR for the ascorbic-acid assisted replacement of Ag by Au at 65°C in ethanol. a) NPs obtained from galvanic replacement of Ag by Au in ethanol, from 0.2Au:Ag (left) to 0.5Au:Ag (right), b-e) corresponding TEM images, and f) normalized extinction spectra. Additional images in Figures SA10 to SA13.

3.3 Temperature Effects on NP Structure
The NP morphology, in particular the smoothness of the shell, is influenced by reaction temperature in alcohols, with 65°C maximizing surface smoothness and minimizing pinholes. Temperature effects for ethanol and methanol are presented in Figures A4 (0.5Au:Ag), SA14, and SA15 (0.2, 0.3, 0.4, 0.5Au:Ag). In methanol at room temperature (Figure A4a), the NPs have a very rough surface, and each particle has at least one apparent pinhole. As the temperature increases to just below methanol’s boiling point (55°C, Figure A4b), the NPs are smoother with fewer pinholes. Eventually, at 65°C, the solvent’s boiling point, the NPs are completely smooth with few to no pinholes (Figure A4c). In ethanol, the overall NP product surface is reproducibly rougher than in methanol across all temperatures (Figures A4d and f). NPs synthesized under the boiling point of ethanol, i.e. at 65°C, are smoother and have fewer pinholes than those synthesized at its boiling point (78°C, Figures A4e and f). The final void size observed by TEM, related to completion of the replacement reaction, appears to be independent of reaction temperature. Equivalent effects, including the production of the smoothest NPs at 65°C for both solvents, were observed for 0.2Au:Ag, 0.3Au:Ag, and 0.4Au:Ag (Figures SA14 and SA15).
Figure A4. Temperature effects on shell morphology. Representative TEM images of the products of 0.5Au:Ag galvanic replacement in methanol performed at a) room temperature (RT), b) 57°C, and c) the solvent’s boiling point, 65°C. Representative TEM images of the products of 0.5Au:Ag galvanic replacement in ethanol performed at a) room temperature, b) 65°C, and c) the solvent’s boiling point, 78°C. *denotes the reaction temperature yielding smooth shells, 65°C for both solvents. Red arrows indicate examples of pinholes. Additional images in Figures SA16 to SA31.

### 3.4 Composition of AgAu Semi-Hollow NPs and Nanoshells

The ascorbic acid-assisted galvanic replacement of Ag NPs by Au produces alloy NPs with composition dictated by the reaction stoichiometry. Energy dispersive X-ray spectroscopy (EDS) point spectra and linescans of 0.2Au:Ag and 0.5Au:Ag samples prepared in methanol (Figures A5 and SA32) confirm that the particles are composed of both Ag and Au. The high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) intensity trace shows the location and projected shape of the void as well as the location of the separation between the two NPs (Figure A5b and d); HAADF-STEM images (e.g., Figure A5a and c) show no indication of
segregated or core/shell structures. Composition analyses for 0.2Au:Ag based on the EDS linescan in Figure A5 reveal that the atomic composition varies from 50% to 95% for Ag and 5% to 50% for Au throughout the NP; the highest Au concentration is found near the NP surface. The NPs from 0.5Au:Ag (Figure A5c) are essentially fully hollow, as evidenced in the HAADF-STEM intensity profile in Figure A5d. The HAADF-STEM image reveals homogeneous contrast of the shell and the EDS line scan indicates an alloy with uniform composition around 74% Ag and 26% Au. The increase in Au relative to Ag with increased Au$^{3+}$ added during the reaction confirms that this approach to galvanic exchange, using co-reduction, leads to facile composition tuning.

Figure A5. Composition profile of semi-hollow and hollow NPs. HAADF-STEM images of two a) 0.2Au:Ag and c) 0.5Au:Ag NPs synthesized in methanol, b,d)
corresponding HAADF-STEM intensity line profile as well as composition profiles from EDS, along the green lines in a and c.

In a previous report,\textsuperscript{308} we demonstrated that in the absence of pinholes, voids in semi-hollow NPs can be reconfigured through beam-driven water radiolysis. We have a continued interest in this type of reaction, and observed that reconfiguration, albeit rare, is possible in NPs with methanol-filled voids that are free of apparent pinholes (Figure SA33). Additional work is underway to understand the radiolysis-driven reactions in trapped non-aqueous liquids.

4. Conclusion

Galvanic replacement of large plasmonic Ag NPs by Au in non-aqueous solvents, namely methanol, ethanol, and DMF:toluene was developed. The reaction was assisted by co-reduction by ascorbic acid in order to overcome the dealloying process that takes place in traditional galvanic replacement. Regardless of particle size, shape, and crystallinity, the products obtained with the optimized reaction conditions were semi-hollow to hollow alloys; with solvent-dependent roughness attributed in part to the relative rates of galvanic replacement and co-reduction. Temperature studies in both solvents indicate an optimal temperature (65°C) to produce smooth shells in methanol and ethanol. The concentration studies performed demonstrate the tunability of both the alloy composition as well as the shell thickness of the semi-hollow and hollow products. This new synthetic strategy has significant implications for galvanic replacement of large, anisotropic NPs,
enabling LSPR tuning in non-aqueous environments, as well as expanding the number of hollow plasmonic nanostructures that could carry a water-insoluble cargo. Furthermore, this approach can utilize the well-established aqueous syntheses of Ag NPs, adding opportunities for shape and size control much beyond that of current organic solvent syntheses, with applications in plasmon tuning in both near and far field. Finally, the synthetic route developed here can be applied to galvanic replacement of air- and water-sensitive metals.

5. Funding Acknowledgement

This research was supported by a 3M Non-Tenured Faculty Award and the American Chemical Society Petroleum Research Fund under grant number 56256 DNI5. S.M.R. wishes to acknowledge financial support from a National Science Foundation Graduate Research Fellowship #1450681. The authors wish to acknowledge support from the Electron Microscopy Center and the Shared Equipment Authority at Rice University.

6. Experimental Methods and Supporting Information

6.1 Chemicals and Materials

Trisodium citrate (C₆H₅Na₃O₇ • 2H₂O, 99.0%) was purchased from J.T. Baker. Silver nitrate (AgNO₃, ≥99.0%), sodium borohydride (NaBH₄, ≥98.0%), polyvinylpyrrolidone MW10,000 (PVP10), methanol (CH₃OH, ≥99.8%), Gold(III) chloride hydrate (HAuCl₄ • xH₂O, 99.999%), and L-ascorbic acid (C₆H₈O₆, reagent
grade) were all purchased from Sigma Aldrich. Ethanol (C₂H₅OH, 200 proof) was purchased from Decon Labs, Inc.

6.2 Synthesis of Ag Precursor

The Ag NP synthesis was adapted from a previously published seed growth method. Seeds were prepared in a 250 mL round bottom flask by heating trisodium citrate (20 mL, 1 wt%) in nanopure water (75 mL) to 70°C under vigorous stirring. Once 70°C was reached, freshly prepared solutions of silver nitrate (1.7 mL, 1 wt%) and sodium borohydride (0.20 mL, 1 wt%) were added quickly in succession. The resulting solution was stirred for 30 minutes, after which it was cooled to room temperature; nanopure water was added such that the final product volume was 100 mL before storage at 4°C overnight. Two discrete growth steps were employed to obtain Ag NPs of the desired size. The previously prepared seed solution (15 mL) as well as trisodium citrate (2.0 mL, 1 wt%) were added to nanopure water (75 mL). This was heated to reflux under vigorous stirring. Upon reaching reflux conditions, fresh AgNO₃ was added (1.7 mL, 1 wt%) and the reaction was allowed to proceed for 60 minutes before being cooled to room temperature. During the second growth step, the same procedure was repeated with an aliquot from the first growth solution (12.5 mL) and more AgNO₃ (2.0 mL, 1 wt%) in nanopure water (75 mL).

6.3 Galvanic Replacement in Alcohols
Ag NPs (1.33 mM) were centrifuged at 6.5×g for 6 minutes and the aqueous supernatant was removed. The NPs were then redispersed in a solution of PVP10 (75 µM) in methanol or ethanol. The particles were diluted to a final concentration of 0.05 mM with the same PVP10 solution. The diluted Ag NP template was prepared for replacement with varying molar equivalents of Au (0.2, 0.3, 0.4, and 0.5Au:Ag) by adding aliquots (6.0 mL) to separate scintillation vials under stirring at 900 rpm. For galvanic replacement including co-reduction, a solution of ascorbic acid (6 mM) was also prepared in methanol and ethanol, and added to each reaction vial in varying amounts: 0.96, 1.44, 1.92, and 2.4 mL, to 0.2Au:Ag, 0.3Au:Ag, 0.4Au:Ag, and 0.5Au:Ag, respectively. Gold(III) chloride hydrate (0.025 M) was freshly prepared in methanol or ethanol and diluted to the working concentration (0.05 mM), which was then added dropwise in appropriate amounts to each reaction and allowed to react to completion over 2 hours. This process was repeated over varying temperatures for methanol (room temperature, 57°C, and boiling point 65°C) and ethanol (room temperature, 65°C, and boiling point 78°C), as well as without ascorbic acid for both solvents at 65°C.

6.4 Galvanic Replacement in DMF:toluene

Ag NPs (1.33 mM) were centrifuged at 6.5×g for 6 minutes and the aqueous supernatant was removed. The NPs were then redispersed in a solution of PVP10 (75 µM) in a 1:1 mixture of N,N-dimethylformamide and toluene. Aliquots (3.0 mL) were
added to two separate scintillation vials under stirring at 900 rpm. Gold(III) chloride hydrate (0.025 M) was freshly prepared in the 1:1 solvent mixture, diluted to the working concentration (0.05 mM), and then added dropwise in the appropriate amounts to 0.2Au:Ag and 0.5Au:Ag samples. This was allowed to react to completion overnight while stirring, although it was observed that the reaction was nearly complete after two hours.

6.5 Characterization Methods

A Cary 5000 UV-vis spectrophotometer was for bulk extinction spectroscopy. TEM images were obtained on a JEOL 1230 High Contrast TEM operated at 80 kV. HAADF-STEM and STEM EDS line scans were obtained at 300 kV on an aberration corrected FEI Titan Themis3 60-300 S/TEM equipped with a Super-X quad EDS detector.

6.6 Experimental Supporting Figures
Figure SA1. Normalized extinction spectrum and vial of as-prepared Ag NPs used as sacrificial template.
Figure SA2. NPs from galvanic replacement in methanol without co-reduction.  
a) NPs obtained from galvanic replacement of Ag in Au in methanol, from 0.2Au:Ag (left) to 0.5Au:Ag (right), b, c) TEM images for 0.2Au:Ag nanocages and 0.5Au:Ag dealloyed Au, and d) corresponding normalized extinction spectra.
Figure SA3. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in DMF:toluene with 0.2 Au:Ag at room temperature.

Figure SA4. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in DMF:toluene with 0.5 Au:Ag at room temperature.
Figure SA5. Vials of the DMF:toluene products. Left, 0.2 Au:Ag, right, 0.5 Au:Ag.

Figure SA6. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.2 Au:Ag at 65°C.
**Figure SA7.** Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.3 Au:Ag at 65°C.

**Figure SA8.** Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.4 Au:Ag at 65°C.
Figure SA9. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.5 Au:Ag at 65°C.

Figure SA10. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.2 Au:Ag at 65°C.
Figure SA11. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.3 Au:Ag at 65°C.

Figure SA12. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.4 Au:Ag at 65°C.
Figure SA13. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.5 Au:Ag at 65°C.
Figure SA14. Temperature effects on the galvanic replacement of Ag by Au in methanol with 0.2 to 0.5Au:Ag at a-d) room temperature, e-h) 57°C, and i-l) methanol’s boiling point, 65°C.
Figure SA15. Temperature effects on the galvanic replacement of Ag by Au in ethanol with 0.2 to 0.5Au:Ag at a-d) room temperature, e-h) 65°C, and i-l) ethanol’s boiling point, 78°C.

Figure SA16. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.2 Au:Ag at room temperature.
Figure SA17. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.3 Au:Ag at room temperature.

Figure SA18. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.4 Au:Ag at room temperature.
Figure SA19. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.5 Au:Ag at room temperature.

Figure SA20. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.2 Au:Ag at 57°C.
Figure SA21. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.3 Au:Ag at 57°C.

Figure SA22. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.4 Au:Ag at 57°C.
Figure SA23. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in methanol with 0.5 Au:Ag at 57°C.

Figure SA24. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.2 Au:Ag at room temperature.
Figure SA25. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.3 Au:Ag at room temperature.

Figure SA26. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.4 Au:Ag at room temperature.
Figure SA27. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.5 Au:Ag at room temperature.

Figure SA28. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.2 Au:Ag at 78°C.
Figure SA29. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.3 Au:Ag at 78°C.

Figure SA30. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.4 Au:Ag at 78°C.
Figure SA31. Additional TEM images of nanoparticles obtained from the galvanic replacement of Ag by Au in ethanol with 0.5 Au:Ag at 78°C.
Figure SA32. EDS spectra from a point on the line scan for a) semi-hollow NPs (0.2Au:Ag) and b) nanoshells (0.5Au:Ag) synthesized in methanol.
Figure SA33. Reconfiguration observed in a pinhole-free, 0.2Au:Ag semi-hollow NP synthesized in methanol. Red points show where the 80 kV scanning transmission electron microscope (STEM) probe was positioned for 10 s prior to acquiring the next high angle annular dark field (HAADF) STEM image.
References


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71. Onuferko, J. H.; Woodruff, D. P.; Holland, B. W., LEED Structure Analysis of the Ni(100) (2x2)C (p4g) Structure; A Case of Adsorbate-Induced Substrate Distortion. Surf. Sci. 1979, 87, 357-374.


212. Woehl, T. J.; Evans, J. E.; Arslan, I.; Ristenpart, W. D.; Browning, N. D., Direct in situ determination of the mechanisms controlling nanoparticle nucleation and growth. *ACS Nano* 2012, 6, 8599.


223. Noh, K. W.; Dillon, S. J., Morphological changes in and around Sn electrodes during Li ion cycling characterized by *in situ* environmental TEM. *Scripta Mater.* **2013**, *69*, 658.


240. Stevens, A.; Yang, H.; Carin, L.; Arslan, I.; Browning, N. D., The potential for Bayesian compressive sensing to significantly reduce electron dose in high-resolution STEM images. *Microscopy* 2014, 63, 41.

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286. Li, J.; Murphy, E.; Winnick, J.; Kohl, P. A., Studies on the cycle life of commercial lithium ion batteries during rapid charge-discharge cycling. J. Power Sources 2001, 102, 294-301.


