August 2018

DESIGN AND SYNTHESIS OF STAINLESS-STEEL NANOPARTICLES: OXIDATION BEHAVIOR AND MORPHOLOGICAL EVOLUTION

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Abstract

The objective of my graduate research is to understand the oxidation in heterostructured transition metal-based core/alloy nanostructures and to design protocol towards the synthesis of oxidation resistant stainless-steel nanoparticles. To this effect, I employed bottom-up wet chemistry approach to synthesize multi-shell Fe/Cr$_x$Ni$_{1-x}$ NPs, bimetallic Fe$_x$Cr$_{1-x}$ alloy NPs, and Fe/Ni core/shell NPs. I performed the morphological analysis of these NPs via transmission electron microscopes (TEM/HRTEM), structural characterization via X-ray diffraction (XRD), surface analysis via X-ray photoelectron spectroscopy (XPS), thermal property analysis via thermogravimetric analysis (TGA), organic ligand characterization using infrared spectroscopy (FTIR), and absorption spectra using UV-visible spectroscopy (UV-Vis). In chapter 2, synthesis of mixed shell Fe/Cr/Ni, Fe/Ni/Cr, and Fe/Cr$_x$Ni$_{1-x}$ core/alloy nanoparticles (CA-NPs) is investigated, where chromium and nickel carbonyl-based precursors are used for depositing various shell combinations. Oxidation in these NPs is studied as a function of shell thickness and shell-deposition routes, and diffusion data for Fe/Cr, Fe/Ni, and Fe/CrNi core/shell NP systems is provided. In chapter 3, I describe the synthesis of cube-shaped Fe$_x$Cr$_{1-x}$ alloy NPs, oxidation and the subsequent formation of internal voids. HRTEM images of oxidized alloy NPs are analyzed to understand the extent of internal void formation as a function of oxidation conditions. In chapter 4, I explore how grain boundary diffusion and interfacial thermodynamics dictates the alloying of core-shell nanoparticles as a function of annealing temperature. The importance of interfacial effects on thermodynamics and diffusion kinetics is described and examined in light of the observed temperature dependent alloying of synthesized $\alpha$-phase Fe/Ni nanoparticles, into $\gamma$-phase Fe/Fe$_x$Ni$_{1-x}$ core alloy nanoparticles. In final chapter, I summarize the research, discuss the scope and future prospects in this research area.
DESIGN AND SYNTHESIS OF STAINLESS-STEEL NANOPARTICLES: OXIDATION BEHAVIOR AND MORPHOLOGICAL EVOLUTION

by

Laxmikant Pathade

B. Tech., Institute of Chemical Technology, Mumbai (2013)

Dissertation

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<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>acac</td>
<td>acetylacetonate</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>Au-NPs</td>
<td>Gold Nanoparticles</td>
</tr>
<tr>
<td>b.c.c.</td>
<td>Body Centered Cubic</td>
</tr>
<tr>
<td>B.E.</td>
<td>Binding energy</td>
</tr>
<tr>
<td>CA-NPs</td>
<td>Core/Alloy nanoparticles</td>
</tr>
<tr>
<td>CdSe</td>
<td>Cadmium Selenide</td>
</tr>
<tr>
<td>CMT</td>
<td>Cabrera-Mott Theory</td>
</tr>
<tr>
<td>d&lt;sub&gt;c&lt;/sub&gt; / d&lt;sub&gt;core&lt;/sub&gt;</td>
<td>Core diameter</td>
</tr>
<tr>
<td>DDA</td>
<td>Discrete Dipole Approximation</td>
</tr>
<tr>
<td>DOE</td>
<td>Dioctylether</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>E&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Bandgap</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>f.c.c.</td>
<td>Face Centered Cubic</td>
</tr>
<tr>
<td>α-Fe-NPs</td>
<td>b.c.c. Iron Nanoparticles</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;x&lt;/sub&gt;Cr&lt;sub&gt;1-x&lt;/sub&gt;</td>
<td>Iron-Chromium alloy with Fe atomic ratio x% &amp; Cr atomic ratio (1-x)%</td>
</tr>
<tr>
<td>E&lt;sub&gt;F&lt;/sub&gt;</td>
<td>Fermi Energy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maxima</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>HDA</td>
<td>Hexadecylamine</td>
</tr>
<tr>
<td>HDACl</td>
<td>Hexadecylammonium chloride</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution TEM</td>
</tr>
<tr>
<td>HT</td>
<td>High temperature</td>
</tr>
<tr>
<td>LCAO</td>
<td>Linear Combination of Atomic Orbitals</td>
</tr>
<tr>
<td>M₃O₄</td>
<td>mixed metal-oxide</td>
</tr>
<tr>
<td>(Ni(CO)₂(PPh₃)₂)</td>
<td>bis(triphenylphosphine)dicarbonyl Nickel (0)</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>OAm</td>
<td>Oleylamine</td>
</tr>
<tr>
<td>ODE</td>
<td>1-octadecene</td>
</tr>
<tr>
<td>QDs</td>
<td>Quantum Dots</td>
</tr>
<tr>
<td>QRs</td>
<td>Quantum Rods</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface Plasmon Resonance</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TOP</td>
<td>Triocylphosphine</td>
</tr>
<tr>
<td>tₛ</td>
<td>Shell Thickness</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>UV-Visible Spectrophotometry</td>
</tr>
<tr>
<td>Vₘ</td>
<td>Mott Potential</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>Powder X-ray Diffraction</td>
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</table>
Chapter 1

Introduction

1.1 Introduction to Nanoparticles

Early 20\textsuperscript{th} century was a time of ambitious discoveries in the field of metal-based materials. Improvements in high-strength alloys and steels resulted in building of skyscrapers, factories, and transportation infrastructure connecting those, ultimately paving the way for the new millennium. In late 20\textsuperscript{th} and 21\textsuperscript{st} century, the latest iteration of same phenomenon has witnessed materials scientists pushing the limits of physics in efforts to make everything around us as small as possible.\textsuperscript{1,2} This is where nanoparticles and the field of nanotechnology come into the picture. Nanoparticles are materials with dimensions between 1 nm to 100 nm.\textsuperscript{3–10} Nanotechnology lies at the intersection of scientific disciplines of chemistry, material science, physics, and biology. Chemists and material scientists are interested in the synthesis aspects and work towards creating materials with novel structure-property relationships, while biologists are utilizing these advances for therapeutic applications, whereas the physicists are occupied with calculating/controlling the electronic and magnetic properties of such materials.

The interest in studying and utilizing novel materials is not new, in fact, the alchemists of the roman era knew that the optical properties of noble metals change when crushed to very fine sizes. They utilized this knowledge for decorative purposes, as exemplified by the famous Lycurgus cup where very fine gold and silver particles are intercalated in glass matrix to achieve dichroic effect.\textsuperscript{11} In 1870, Michael Faraday synthesized and studied colloidal gold NPs,\textsuperscript{12} but the research in the field mostly stayed stagnant. Scientific interest was renewed in 1971 after the famous “There's plenty of room at the bottom” talk by Richard Feynman.\textsuperscript{13} Contemporary
advances in spectroscopic and microscopic characterization methods enabled the analysis of these new materials. National Nanotechnology Initiative (NNI), created by the US govt. in 2001, spent more than $23 billion in research funding and infrastructure,\textsuperscript{14,15} which resulted in an exponential growth in the field of nanotechnology with discovery of novel nanomaterials such as graphene and carbon nanotubes,\textsuperscript{16–20} molybdenum disulfide (MoS\textsubscript{2}),\textsuperscript{21,22} two-dimensional Gallium Nitride (GaN),\textsuperscript{23,24} metal nanoparticles,\textsuperscript{25–29} semiconductive quantum dots (QDs),\textsuperscript{30–35} with wide array of structures and properties, and has changed the fundamental way we think about nanomaterials.\textsuperscript{36}

Over the next chapter I define nanomaterials and present a general overview of the field describing their physical properties, changes in physical properties at the nanoscale, and their applications in section 1.1. I discuss bottom-up and top-down methods for nanoparticle synthesis in section 1.2. Nanoparticles with core/shell & core/alloy morphologies are introduced in Section 1.3, and diffusion between the core and the shell materials is discussed. In section 1.4, I describe Kirkendall diffusion, and subsequent oxidation and void formation at the core/shell interface. Finally, section 1.5 details the objective and scope of this dissertation.

**1.1.1 Physical Properties at the Nanoscale**

Physical properties of nanomaterials differ vastly from that of bulk samples of the same material and exhibit a selection of interesting characteristics. For example, while bulk gold has a lustrous yellow color, gold nanoparticles (Au-NPs) absorbs green light ($\lambda_{\text{abs}} = \sim 520 \text{ nm}$) and appear red in color. Another example shows that noble metal NPs are few thousand times more efficient catalysts than bulk counterparts.\textsuperscript{37} These changes in physicals and chemical properties at the nanoscale occur due to scalable and quantum effects, where scalable effects arise due increase in surface atom fraction, whereas quantum effects are seen due to energy level discretization.\textsuperscript{38–45}
a cluster, surface atoms behave differently than the inner atoms, and as the size of cluster reduces, surface to volume ratio of the material changes dramatically, leading to enhanced scalable effects.\textsuperscript{40,41} Fraction of surface atoms may be approximated by:\textsuperscript{46,47}

\[ N_S = 4 \times N^{-1/3}, \]

where \( N \) is the total number of atoms in the nanoparticle.

Figure 1.1(a) shows that as the number of atoms decreases the fraction of surface atoms increase. For example, in case of face centered cubic packed gold nanoparticles, an Au-NP with diameter of 2 nm has \(~64\%\) atoms at the surface, a 50 nm Au-NP will have 2.5\% surface atoms, whereas a 10 \( \mu \)m particles will only have less than 0.01\% atoms on the surface. High percentage of surface atoms is observed in a HRTEM image of CdSe QDs (\( d_{\text{core}} = \sim 7 \) nm) in Figure 1.1(b).

\textbf{Figure 1.1.} Plot shows the surface area to volume ratio and fraction of surface atoms as a function of decreasing nanoparticle diameter (a). Surface atoms are visible on a high-resolution TEM image of CdSe quantum dots (b).

In 1937, Herbert Fröhlich studied specific heat of smaller particles at low temperatures, and proposed that smaller particles have discrete electronic states.\textsuperscript{42} Few years later in 1962, Ryogo Kubo proved theoretically that this discretization of energy states will affect the electronic
properties of the fine particles. Reduction in the total number of atoms results in quantization of energy levels, changing the band structure and the density of states of the new ensemble. Conversely - going from single atom to a cluster - linear combination of atomic orbitals (LCAO) approach may be employed to obtain the new band structure for the cluster. As the bandgap $E_g$ between the valence and conduction bands increases, materials transition from conductors ($E_g \approx 0$ eV), to semiconductors ($0 \text{ eV} < E_g < 4.5 \text{ eV}$), and finally to insulator ($E_g > 4.5 \text{ eV}$). Fermi energy ($E_F$) is the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (LUMO) at absolute zero. Kubo gap ($\delta$) is a similar measure of the average energy difference between the consecutive electronic states in materials with quantized energy states, and is associate with Fermi energy by,$^{40,44,47}$

$$\delta = 4 \times \frac{E_F}{3N}$$

where $E_F$ is the Fermi energy and $N$ is the number of energy levels. Table 1.1. lists the Kubo gap in Na atomic cluster as the function of diameter.
Figure 1.2. Transition from bulk to microscopic sizes lead to increase in the band gap or the Kubo gap. (Reproduced with permission from ref\textsuperscript{40})

Table 1.1. Percentage of surface atoms, surface energy, Kubo gap for Na atom clusters of given diameters.\textsuperscript{6,46,47,49}

<table>
<thead>
<tr>
<th>NP diameter (nm)</th>
<th>Surface Atoms (%)</th>
<th>Surface Energy (J/g)</th>
<th>Kubo gap (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>560</td>
<td>5000</td>
</tr>
<tr>
<td>2</td>
<td>63.71</td>
<td>280</td>
<td>625</td>
</tr>
<tr>
<td>3</td>
<td>42.47</td>
<td>186.67</td>
<td>185.19</td>
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1.1.2 Changes in Physical Properties due to Scalable and Quantum Effects

As suggested by the Kubo model, decrease in the particle size results in quantized electronic states and quantum effects become evident. Semiconductive quantum dots (QDs) nanocrystals, which typically have 2-10 nm diameters, are a good candidate to explain the discretization of energy levels.\textsuperscript{50,51} Since the QDs radius is smaller than the corresponding bulk Bohr-Exciton radius, the electron-hole pair is confined within the nanocrystal and adheres to a “particle in box” model. Solving the quantum mechanical equations for this system shows that changing the radius of the semiconductive quantum dots, the bandgap may be tuned.\textsuperscript{52,53} For CdSe QDs, for example, a diameter 10 nm will result in band gap of 1.9 eV, while for a nanocrystal with a diameter of 1.2 nm, the bandgap will be ~3 eV.\textsuperscript{54} Bulk gold is very often thought of as one of the better conductors of electricity, and this is true even for Au-NPs, but when Au-NPs with diameter of ~1 nm are synthesized, a transition from metallic to semiconductive nature is observed.\textsuperscript{55,56}

Optical properties of NPs are strongly aligned with their shapes, sizes, composition, and surrounding dielectric media.\textsuperscript{57–61} Surface plasmon resonance (SPR) phenomenon is observed in metallic NPs when delocalized conduction band electrons at the surface are excited by incident electromagnetic waves and resonate at the particular wavelengths.\textsuperscript{62} In Au-NPs, for example, the mean free path is ~50 nm and energy above this threshold causes surface plasmons to resonate at specific wavelengths resulting in a standing wave around the NP, and is responsible for red color ($\lambda_{\text{abs}} = ~520$ nm) of Au-NPs.\textsuperscript{51,63} Our previous work showed that absorption characteristics of Au$_x$Ag$_{1-x}$ alloy NPs can be controlled by tuning the ratio of the composition.\textsuperscript{64–68} Mie theory\textsuperscript{69} and Discrete Dipole Approximation have made it easier to calculate the absorption and scattering around valid and hypothetical nanoparticle geometries. Discrete Dipole Approximation is a
flexible & powerful simulation technique used to calculate the scattering and absorption of electromagnetic spectrum by targets with arbitrary geometries and complex refractive index.\textsuperscript{70–72}

Quantum-size effects also affect the thermodynamic properties of metallic nanoparticles.\textsuperscript{45} An increase in the percentage of surface atoms lowers the melting temperature of nanoparticles.\textsuperscript{73,74} In 1992, Alivisatos and colleagues showed that CdSe semiconductor nanocrystals exhibited large depression in melting temperature as the size decreases.\textsuperscript{75} This alters the alloy phase diagrams in such a way that temperatures required for phase transition are lowered by few hundred degrees. This was seen in our alloy Fe/Fe\textsubscript{1-x}Ni\textsubscript{x} core/alloy NP system where a we observed that the phase transition to \(\gamma\)-phase transition occurs at relatively low temperature of 200 \(^\circ\)C (chapter 4). Surprising properties such as negative heat capacity have also been experimentally observed.\textsuperscript{77}

While not a nanomaterial, Raney Nickel has been used for past 90 years as a catalyst due to its relatively higher surface area than bulk Ni for given volume.\textsuperscript{77} NPs are typically more efficient catalysts as higher surface area allows for increased reactivities.\textsuperscript{78–83} Moreover, hollow or porous NPs are more even more efficient as catalysts.\textsuperscript{83–85} Within a single nanoparticle, different facets may have differing activities due to their respective surface binding energies. Xia and colleagues showed that high index Pt-NP & Pd-NP show an increase in catalytic activity.\textsuperscript{86–88} Catalytic activity varies strongly even in case of a tiny cluster size changes, as shown in case of platinum cluster.\textsuperscript{89}

\textbf{1.1.3 Overview of Applications of Nanomaterials}

There’s significant interest in commercializing inventions in the field of nanotechnology,\textsuperscript{90–93} and industrial scale manufacturing of NPs has started in past decade.\textsuperscript{94,95}
Several studies describe the cost effectiveness of NPs over traditional methods, and NPs are being integrated in consumer products. With the strong growth in the adaption of electric vehicles in the United States, research in the field of nanomaterial-based energy storage and energy conversion devices has picked up pace. Research includes development of hollow nanoparticles for Li storage, nanoelectrodes, photovoltaics, cathode materials, nanostructured anode materials for efficient storage of lithium in new age Li-sulfur, and Li-air batteries; even biological electrodes based on self-assembled viruses have been synthesized. Novel lead based CH$_3$NH$_3$PbX$_3$ & CsPbX$_3$ perovskite nanocrystals have brought about exciting improvements as charge transport materials for photovoltaic applications. Long range, near perfect perovskite crystal structures means low defect concentration makes the perovskite materials highly efficient light absorbers as well as charge carriers for solar cells. Moreover, by tuning the composition (by means of simply varying the halide anion concentration within the perovskites), their optoelectronic properties may be tuned for emission over the complete range of visible region of the EM spectrum.

Moore’s law suggests that the number of components on electronics circuit will double every year (i.e. size of transistors and circuit components will decrease by 50%) and this has worked out surprisingly well for past 4 decades. Smaller sizes not only means faster computing, it also mean low energy consumption and less heat generation. However, in past few years, limitations of physics are catching up to the it, with transistor size decreasing from 10 µm in 1970s to 1 nm in 2017. Atomic-scale memory have been achieved at silicon surface, where central atom is used to store memory while surrounding atoms prevent interactions from adjacent atoms.
Nanoparticle based catalysts, have been synthesized using various metals including Au-NPs,\textsuperscript{158} Cu-NPs,\textsuperscript{159} Pt-NPs,\textsuperscript{160–163} and more.\textsuperscript{78–86} Using hollow and porous nanoparticle for gas storage has been discussed in detail by Morris and Wheatley.\textsuperscript{164,165} Many nanoparticle based high performance chemicals sensors have been synthesized.\textsuperscript{166–169} Examples include a ‘chemical nose’ sensor for identification of proteins,\textsuperscript{175–178} Qdots in chemical and biological sensing,\textsuperscript{170} and CsPbX\textsubscript{3} perovskites for halide identification.\textsuperscript{146,147}

Nanoparticles have been employed in bio-medical fields\textsuperscript{169} for medical imaging,\textsuperscript{170–173} medicines,\textsuperscript{174} drug delivery,\textsuperscript{176–181} and biodiagnostics.\textsuperscript{181} Our previous work has shown that cancer drugs such as Doxorubicin may be delivered effectively using functionalized Au-NPs.\textsuperscript{182–184} El-Sayed and colleagues have extensively studied optical properties & functionalization of Au-NPs for cancer drug delivery.\textsuperscript{185–188} Silica coated ferromagnetic Fe\textsubscript{3}O\textsubscript{4} NPs have been used to deliver ibuprofen,\textsuperscript{177} platin,\textsuperscript{175} cisplatin,\textsuperscript{176} and additional cancer drugs.\textsuperscript{178,179}

\section*{1.2 Synthesis of Nanoparticles: Top-Down and Bottom-Up Methods}

Over past few decades, nanoparticle synthesis has gone through tremendous changes and numerous methods exist to obtain nanoparticles.\textsuperscript{3–10,125} These methods are generally divided into two groups, namely, top-down methods and bottom-up methods.\textsuperscript{189} As implied from the names, top-down methods involve breakdown of large precursor block and is very much like the traditional milling methods. Top-down methods are typically physical vapor deposition methods such as arc discharge,\textsuperscript{190} focused ion beam sputtering,\textsuperscript{191,192} inert gas condensation,\textsuperscript{193,194} and laser ablation.\textsuperscript{195,196} Common theme for these methods is layered milling of top surface using high-energy radiations, which typically require highly specialized expensive setup. Use of very specific
protocols however allow high precision in product and thus top-down methods are often employed in semiconductor chip manufacturing industry.

Bottom-up approach is closer to traditional wet-chemistry methods where reactants are mixed at relatively milder conditions to obtain larger assembled structure in small batches. Synthetic methods typically involve chemical reduction of metal salts at high temperatures,\textsuperscript{197–201} solvothermal synthesis,\textsuperscript{202} sonochemical synthesis,\textsuperscript{203,204} photochemical synthesis,\textsuperscript{205–207} electrochemical synthesis,\textsuperscript{208–210} high-temperature decomposition / thermolysis / hot-injection methods,\textsuperscript{211,212} and reverse micelle based template synthesis\textsuperscript{213,214}. This approach is relatively low cost, versatile, and new synthesis could be started with minor alterations to the whole setup. While use of Schlenk-lines, round-bottom flasks, and gloveboxes is common, microwave reactors have also been employed. Quantum dots were synthesized using microwave reactors with variable size and photo-physical properties\textsuperscript{215}.

Attempts to ‘print’ nanostructures have been made, for example, in 1999, Mirkin and colleagues developed Dip-pen Nanolithography, where they were able to “write” (deposit) a 30 nm thin layer of alkanethiol molecules on Au film.\textsuperscript{216} Another approach to create large scale NP networks involves utilization of assembly behavior in modified NPs. DNA origami and DNA-mediated rational assembly of NPs (QDs and Au-NPs) has improved the efficiency of aggregating the synergistic effects of NPs into an assembled macrostructure\textsuperscript{217–231}.

1.3. Core/Shell and Core/Alloy Nanoparticle Morphologies

Core/Shell nanoparticles are novel nanostructures that synthesized by layered deposition of shell material on the previously synthesized core sample. Such heterostructured nanocomposites synergistically combine the physical properties of both the core and the shell materials and thus,
are increasingly employed over materials with single component. Performance of these multicomponent materials is determined by individual properties of the components and their interface. The shell material can contribute towards altering the optical,\textsuperscript{193} magnetic,\textsuperscript{55,77} and structural properties\textsuperscript{235} of the core, and thus hold special interest for a solid state chemist. A quick search of the term ‘core shell nanoparticles’ on \textit{Web of Science} repository shows us the increased interest in the topic over past two decades. Our group’s research on core/shell and core/alloy NP systems has resulted in peer reviewed publications on localized surface plasmon resonance (LSPR) attenuation,\textsuperscript{64} optical property tuning,\textsuperscript{65–67} asymmetric growth,\textsuperscript{236} novel stainless Fe/FeCr core/void/shell NPs,\textsuperscript{237} superparamagnetic Fe/Ni core/shell etc. Recently, novel Fe/Cr, Fe/Ni, Fe/Cr/Ni, nanoparticles with core/void/shell morphology were synthesized by the Maye research group.\textsuperscript{237–241} These composite core/shell nanoparticles, may be employed as sacrificial templates for layered structures,\textsuperscript{242,243} and could be tailored for applications in bioimaging,\textsuperscript{244,245} catalysis,\textsuperscript{246,247} and electrodes for Li\textsuperscript{+} ion batteries.\textsuperscript{248–250}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{pubs.png}
\caption{Number of hits for the search term ‘core shell nanoparticles’ in the \textit{Web of Science} database over past 2 decades.}
\end{figure}
1.3.1. Synthesis of Core/shell Nanoparticles via High Temperature Decomposition Methods

One of the preferred methods for the synthesis of core/shell NPs involves high-temperature decomposition (~200 °C) and of the precursors in presence of organic solvents, ligands under inert conditions. Typical synthesis yields several milligrams to few grams of NP product per batch. Figure 1.4 shows the typical synthetic protocol for the synthesis of Fe/Cr Core/shell NPs.

![Synthesis of Core/shell Nanoparticles via High Temperature Decomposition Methods](image)

**Figure 1.4.** A reaction scheme showing synthesis of Fe/Cr Core/shell NPs that involves decomposition of metal precursors Fe(CO)$_5$ to synthesize Fe NPs and then slow decomposition of Cr(CO)$_6$ onto the core seed NPs in presence of organic ligands at high-temperature under oxygen free conditions.

We start with Fe(CO)$_5$, a relatively inexpensive, but volatile metal complex which is commonly employed as a precursor for Fe-NP synthesis.$^{197,251}$ Fe(CO)$_5$ has trigonal bipyramidal structure with low ligand field stabilization energy (LFSE = -12.52·Δ$_5$) and breaks down at 180 °C producing CO gas and Fe atoms that further nucleate to grow body centered cubic (b.c.c.) packed α-Fe NPs. From the Fe phase diagram, phase change from α-Fe (b.c.c.) to γ-Fe (f.c.c.) is expected at higher temperatures (>300 °C). This provides flexibility to choose a specific crystalline packing type, ideal for the core material. Hexadecylamine chloride (HDA·Cl) acts as a capping ligand and slows down the nucleation, and is used during the synthesis of Fe-NPs to improve crystallinity & size uniformity.$^{251}$ Hexadecanediol, oleic acid (OAc), oleylamine (OAm)$^{252,253}$ and trioctylphosphine (TOP)$^{254}$ are some compounds that can be used as surface capping ligands.$^{255}$
Chromium hexacarbonyl (Cr(CO)_6) - a precursor for intended Cr shell - is dissolved in a high boiling organic solvent such as dioctylether (DOE) at moderately high temperatures (100 °C) and injected in the α-Fe NP solution over multiple steps & extended period to ensure complete shell coverage. Annealing during this shell deposition step causes alloying at the core/shell interface forming Fe_xCr_{1-x} alloy, aided by their identical lattice parameter (a = 2.87 Å) and packing type (b.c.c.). Opening the sample to air at low temperature result in oxidation at the NP surface. Here, a thin passivating oxide layer formed by the chromium shell mimics the bulk stainless steel phenomenon and prevents further oxidation of Fe core. But the novelty about this synthesis is that, as the chromium shell gets thinner, we observe the diffusion of Fe core to the surface and formation of voids. Detailed synthesis parameters are discussed in upcoming chapters.

1.3.2 Quantifying Diffusion in Core/Shell NP System to Understand Likelihood of Internal Void Formation
Figure 1.5. Heat map of relative diffusion rates is plotted for binary Host/dopant couples. Void Formation in Binary Core/Shell Systems may be predicted based on relative diffusivities of metal pairs. Red region indicates higher diffusivities and are a better candidate for core material, whereas the blue region metals are preferable as shell materials. Magnitude axis displays interfacial diffusion rate (in cm²/s). Diffusion values not available for grayed-out binary couples.

Figure 1.5 shows the heat map of relative diffusion rates in various binary couples along with further discussion on their void probability, based solely on diffusion rates. Intermetallic diffusion rates of binary couples (Host/Dopant combinations of Al, Ti, Cr, Mn, Fe, Co, Ni, Mo, and W) are typically reported at temperatures >1000 °C, and thus modified Arrhenius equation is used to approximate values at 180 °C.

\[ D = D_0 \times e^{E_D/RT} \]

where \( E_D \) is the activation energy of diffusion, \( R \) is the gas constant, \( T \) is temperature in K, and \( D_0 \) is the frequency factor.

Four diffusion routes are possible in a binary A-B couple, namely, \( A \leftrightarrow A \), \( A \rightarrow B \), \( A \leftarrow B \), and \( B \leftrightarrow B \). To form voids in a core/shell nanoparticle, it is necessary that the outward diffusion rate (\( A \rightarrow B \)) of the core be higher than the rate from the shell to the core (\( B \rightarrow A \)). Tracy et al. showed that when self-diffusion (\( A \leftrightarrow A \)) is significantly higher than outward diffusion (\( A \rightarrow B \)), a single large void is formed (e.g. Ni/NiO), but if outwards diffusion (\( A \rightarrow B \)) is faster than self-diffusion then several smaller, localized voids are formed, which later coalesce, in a similar fashion as the Fe/Cr stainless NPs, (other examples are CoO, CoₓSᵧ, and FeₓOᵧ).²⁵⁶ Self-diffusion rate in the shell (\( B \leftrightarrow B \)) should be minimum to minimize shell rearrangement and thus maintain structural stability. In summary, to improve void formation in core/shell (A/B) NPs, the preferred diffusion patterns should be -

\[ \text{Core} \rightarrow \text{Shell} > \text{Core} \leftrightarrow \text{Core} >> \text{Core} \leftarrow \text{Shell} > \text{Shell} \rightarrow \text{Shell} \]

For Fe/Cr core/shell system, this is found to be true. Brackets show the diffusion rates in cm²/s -
When basing the likelihood of void formation *solely* on the relative diffusion rates of the core and the shell metals, it was found several systems could potentially form core/void/shell morphologies. Metals with high diffusivities (red region) are preferred core materials whereas ones with low diffusion rates (blue) are preferable as shell. Based on diffusion conditions as described above, following core/shell couples were found to have high prospect of forming core/void/shell microstructure -

\[
\text{Ti/Cr, Ti/Fe > Al/Fe > Fe/W > Fe/Mo > Fe/Ni > Fe/Cr > Fe/Co}
\]

Johnson et al\textsuperscript{257} calculated the segregation energies of the binary transition metal couple via density function theory (DFT), and showed that the core/shell preference for these couples. Results in our analysis are based solely on analysis of intermetallic diffusion rates but compare well with their study. Above data should be tested with other variables such as miscibility, segregation energies, and crystal structure to better gauge the likelihood of void formation in core/shell system.

\section*{1.4. Nanoscale Kirkendall Diffusion and Oxidation in Transition Metal Nanoparticles}

Recent research in hollow nanoparticle synthesis reports the use of the Kirkendall diffusion along with galvanic exchange and anion exchange\textsuperscript{258} The Kirkendall effect is a classic alloying phenomenon, which occurs due to the difference in the diffusion rates of materials present at the interface\textsuperscript{259} Different diffusivity of the atoms causes super-saturation of vacancies at the core/shell boundary and further coalescence of these vacancies causes formation of ‘Kirkendall Voids’, resulting in hollow nanocrystals. Kirkendall diffusion may be considered as an undesirable phenomenon at macroscale as it may weaken of the mechanical integrity of the material. At nanoscale, however, these are of great interest because the voids provide even higher surface area
to volume ratios via porosity. It is now considered as one the generic fabrication methods for synthesizing hollow nanocrystals. Sixty years after discovery, the Kirkendall effect is receiving scientific attention for its applications in synthesis of hollow nanostructures.

At the nanoscale, oxidation of core/shell NPs is an interesting topic due to the formation of voids in the core and the shell layers due to Kirkendall effect. While Kirkendall phenomenon does not necessarily have to be an oxidative diffusion process, most research articles discuss the oxidative morphological transformation since the oxidative diffusion process is relatively much faster than metal-metal diffusions. Core/shell NPs with hollow internal morphology are often synthesized by utilizing the Kirkendall diffusion phenomenon. An earlier example of Kirkendall diffusion is oxidation of CoS$_y$ where hollow cobalt nanostructure was formed after oxidative removal of sulfur in form of SO$_2$. Since the CoS$_y$ study, several synthetic approaches have been tried. Kirkendall diffusion has been employed for oxidative transformations of nanocrystals into nanospheres, hollow nanotubes, and colloidal nanocages. In case of Fe/Cr core/shell NPs, it was established that due to the difference between diffusion rates of Fe & O$_2^-$, an outward diffusion of the core ensued.

Oxidation of Fe-NP can yield variety metal-oxide morphologies, which may include completely oxidized solid Fe$_3$O$_4$ NPs, hollow Fe$_3$O$_4$ NPs and Fe/Fe$_3$O$_4$ core/shell NPs. Strain at the oxide interface is known to enhance the NP oxidation rate. Presence of chromium shell prevented the complete hollowing of the core by forming a passivating oxide layer as observed at the macroscale in stainless steel. The Cabrera and Mott theory (CMT) for thin films can be used to understand the chemical transformations at the M-M$_3$O$_4$ NP interface due to ionic and electronic currents. CMT assumes that electrons cannot pass freely from the metal through the metal oxide layer to reduce surface oxygen atoms. The wide band gap of the metal oxide prevents this electron
transfer. Here, diffused Fe core oxidizes at the surface forming an iron oxide layer, which results in slight increase in particle size and potentially a wider band gap (due to the oxide layer). Final product showed a symmetrical void formation between the core and shell interface. We discuss CMT and oxidation in Fe/M (M= Cr, Ni, & respective oxides) systems in further chapters.

1.5. Objectives of this Dissertation

The objective of my graduate research is to understand the oxidation in heterostructured transition metal-based core/alloy nanostructures and to design protocol towards the synthesis of these heterostructured nanomaterials. To this effect, I employed bottom-up wet chemistry approach to synthesize multi-shell Fe/Cr$_x$Ni$_{1-x}$ NPs and bimetallic Fe$_x$Cr$_{1-x}$ alloy NPs & Fe/Ni core/shell NPs. I performed the morphological analysis of these NPs via transmission electron microscopes (TEM/HRTEM), structural characterization via X-ray diffraction (XRD), surface analysis via X-ray photoelectron spectroscopy (XPS), thermal property analysis via thermogravimetric analysis (TGA), organic ligand characterization using infrared spectroscopy (FTIR), and absorption spectra using UV-visible spectroscopy (UV-Vis). In chapter 2, synthesis of mixed shell Fe/Cr/Ni, Fe/Ni/Cr, and Fe/Cr$_x$Ni$_{1-x}$ core/alloy nanoparticles (CA-NPs) is investigated, where chromium and nickel carbonyl-based precursors are used for depositing various shell combinations. Oxidation in these NPs is studied as a function of shell thickness and shell-deposition routes, and diffusion data for Fe/Cr, Fe/Ni, and Fe/CrNi core/shell NP systems is provided. In chapter 3, I describe the synthesis of cube-shaped Fe$_x$Cr$_{1-x}$ alloy NPs, oxidation and the subsequent formation of internal voids. HRTEM images of oxidized alloy NPs are analyzed to understand the extent of internal void formation as a function of oxidation conditions. In chapter 4, I explore how grain boundary diffusion and interfacial thermodynamics dictates the alloying of
core-shell nanoparticles as a function of annealing temperature. The importance of interfacial effects on thermodynamics and diffusion kinetics is described and examined in light of the observed temperature dependent alloying of synthesized α-phase Fe/Ni nanoparticles, into γ-phase Fe/Fe\(_x\)Ni\(_{1-x}\) core alloy nanoparticles. In final chapter, I summarize the research, discuss the scope and future prospects in this research area.
Chapter 2

Understanding the Oxidation Behavior of Fe/FeCrNi Nanoparticles

In this chapter I describe a method to synthesize core/alloy nanoparticles (CA-NPs) based on transition metal alloys with tunable oxidation properties. We investigated the use of chromium and nickel carbonyl-based precursors to control shell deposition and thickness at α-Fe cores producing Fe/Cr/Ni, Fe/Cr/Ni, and Fe/Cr$_x$Ni$_{1-x}$ CA-NPs. We compared the systems by monitoring their resistance to oxidation and found that it is highly dependent on the shell and alloy sequence as well as thickness, with mixed shell Fe/Cr$_x$Ni$_{1-x}$ having the best stainless behavior. The CA-NP growth was monitored by TEM, and composition was assessed XPS. Oxidation was quantified by both powder XRD and XPS. The results were analyzed in light of alloy miscibility and diffusion, as well as lattice strains and interfacial oxidation rates. We also investigate the intermetallic diffusion and oxidation rates at the core/alloy interface in mixed shell CA-NPs. The material contained within this chapter is published$^{238}$ in Journal of Physical Chemistry C (Pathade, L.; Doane, T. L.; Slaton, R. D.; Maye, M. M. Understanding the Oxidation Behavior of Fe/Ni/Cr and Fe/Cr/Ni Core/Alloy Nanoparticles. *J. Phys. Chem. C* 2016, 120 (38), 22035–22044.). This Chapter has been reproduced with permission from J. Phys. Chem. C, 2016, 120 (38), 22035–22044. Copyright © 2011 American Chemical Society.

2.1. Introduction

Controlling the oxidation of metal interfaces is of the same great importance today as it was a half century ago when discoveries related to oxidation theory, diffusion rates, and phase behavior led to advances in super alloys, shape memory alloys, and stainless steels.$^{267,268}$ Today,
research at the interface of metals and metal oxide focuses on technologically important thin-films, and at the optimization of nanoscale metal properties. Research in the field of corrosion science usually focuses on thin film coatings, pitting studies, structural stability, and studying surface layers in stainless steel. Metals such as chromium and nickel have long been a mainstay in the science of corrosion resistance on bulk scale. However, little research have been done to introduce corrosion resistant materials at the nanoscale, and this is especially true for transition metal nanoparticles. Transition metal nanoparticles have recently been used in applications as diverse as water splitting, magnetic data storage, catalysis, and biomedical probes. However, due to the concerns with oxidation stability at the nanoscale, materials researchers often choose to work on metal oxide species rather than pure metals. Not surprisingly, even at the bulk scale, one of the major setbacks associated with transition metals is corrosion, amounting to losses in tunes of billions per year to the economy. Industrial bulk stainless steels typically have FeCr and FeNiCr compositions. While studies of stainless thin films and bulk alloys are well known, the chemical synthesis of these steels at the nanoscale is under-explored. One area that continues to be promising for manipulating NPs is the use of oxidation, and the intricate differences in diffusion rates between transition metals and their oxides, as a synthetic tool to manipulate nanoscale architecture and performance.

Binary transition metal NPs, including Fe/Cr, Fe/Ni, have been synthesized using metal carbonyl precursors. For example, Wang and colleagues synthesized uniform Fe-Mo alloy NPs by thermal decomposition of Fe(CO)₅ and Mo(CO)₆ in presence of capping ligands. Metal carbonyls decompose readily at higher temperatures and owing to their zerovalent metal center, avoid galvanic exchange commonplace in metal salt-based syntheses. Similarly, ternary Co/Mn/P NPs were recently synthesized by decomposing Co₂(CO)₈ and Mn₂(CO)₁₀ with
However, until now the synthesis and studies of ternary metallic core/alloy NPs have typically been limited to noble metal based heterostructures.\(^{37,301,302}\)

The oxidation of a metal surface at low temperature is classically described using Cabrera-Mott (C-M) theory\(^{266}\) and at the nanoscale the same mechanistic considerations can lead to surprising morphological and composition variations. Take for example self-diffusion in iron (\(\alpha\)-Fe), chromium (\(\alpha\)-Cr), and nickel (Ni). At 100 °C, Fe atoms self-diffuse in a b.c.c. lattice at \(2.3 \times 10^{-35}\) \(\text{cm}^2/\text{s}\) but diffuse at \(4.7 \times 10^{-42}\) \(\text{cm}^2/\text{s}\) in Cr, and \(3.0 \times 10^{-37}\) \(\text{cm}^2/\text{s}\) in Ni showing hindered mobility in these metals. Conversely, both chromium and nickel show faster diffusion in Fe relative to self-diffusion. Interestingly, when a surface is only partially oxidized, such diffusion can increase, as in the case of Fe in Fe\(_3\)O\(_4\), or decrease, in the case of Ni in NiO. As oxidation rates depend highly on the electric field generated between absorbed oxygen and the metal (termed the Mott potential), temperature and activation energy for metal (and oxygen) diffusion, the results are expected to be different not only due to shell thicknesses at a NP interface, but also due to the sequence of different metal layers in the protective shell. This divergent diffusion trend leads to Kirkendall effects playing a major role at nano interfaces, particularly during oxidation, which can lead to void formation or NP hollowing.\(^{237,303,258}\) Thus, to a synthetic materials chemist, the careful choosing of material combinations, and reaction conditions (ligand environment, oxygen pressure, annealing temperature, etc.), can lead to new rationally designed NP morphologies, microstructures, and compositions, but tailoring these syntheses requires knowledge of the important factors governing multi-metallic NP oxidation.

In our initial work, we studied diffusion in binary Fe/Fe\(_{x}\)Cr\(_{1-x}\) and multi-metallic Fe/FeCrNi core/alloy NPs, where formation of passivating mixed metal-oxide M\(_2\)O\(_4\) (M= Fe, Cr, Ni) shell layer, analogous to the one in bulk stainless steel, was shown.\(^{237,238,240}\) However, extensive void
coalescence in Fe/Fe$_x$Cr$_{1-x}$ NPs revealed that a significant oxidative Kirkendall diffusion of the $\alpha$-Fe core is necessitated in order to achieve the final ‘stainless’ alloy.\textsuperscript{237} This diffusion proportionately increases the share of metal oxides in the overall NP composition. In order for a structured material to possess truly ‘stainless’ character, it should demonstrate slower core diffusion, low core-to-shell miscibility, slow anionic diffusion ($O^{2-}$), and relatively minimal shell composition. Here we report synthesis of oxidation resistant transition metal nanoparticles with multi-element core/alloy architecture. If successful, nano forms of steel may prove to be especially useful in applications ranging from additive manufacturing, coating, magnetics, and even biotechnology.

In this study we investigate the synthesis and properties of Fe/Cr/Ni, Fe/Ni/Cr, and Fe/Cr$_x$Ni$_{1-x}$ CA-NPs. In the described approach, a metallic alloy interface is deposited at a pre-synthesized $\alpha$-Fe NP core. Deposition occurs via the catalytic decomposition of chromium (Cr(CO)$_6$) and nickel (Ni(CO)$_2$(PPh$_3$)$_2$) precursors under inert conditions. While other synthesis approaches exist for the preparation of core/shell or oxides of these compositions, in this approach, the goal of preparing metallic nanoparticles required the use of zerovalent metal precursors, which allowed us to; (i) overcome challenges presented by redox reactions at the interface (i.e., reduction potentials),\textsuperscript{240} (ii) to promote alloying by adding very thin, to sub-monolayer shells,\textsuperscript{66,65,236} and (iii) to utilize difference in metal diffusion rates to manipulate oxidation properties. We demonstrate that this synthesis approach produces metallic alloy shells, and that not only does shell deposition sequence matter in the final performance of the nanoparticle, but also that thin shells perform better than thick shells in many instances. Performance was evaluated by the ability of the CA-NPs to resist oxidation at elevated temperatures and was followed by powder X-ray diffraction (XRD),
and X-ray photoelectron spectroscopy (XPS). The results were considered in light of alloy diffusion and oxidation rates, which were compared to and modeled for the nano interfaces.

2.2. Experimental

2.2.1. Chemicals: Iron (0) pentacarbonyl (Fe(CO)$_5$, 99.5%), (bistriphenyphosphine)dicarbonyl nickel (0) (Ni(CO)$_2$(PPh$_3$)$_2$, 98% anhydrous), chromium (0) hexacarbonyl (Cr(CO)$_6$, 99%), oleylamine (OAm, 70%), 1-octadecene (ODE, 90%), dioctylether (DOE, 99%), tetrahydrofuran (THF, anhydrous, ≥99.9%), hexadecylamine (HDA, 90%), hydrochloric acid (HCl, 1.0 M in diethylether), hexanes (95%) and ethanol (EtOH, 200 proof) were purchased from Sigma-Aldrich and used without further purification.

2.2.2. Synthesis of Fe/FeCrNi NPs

Fe/FeCrNi NPs were synthesized by slow deposition of Cr & Ni precursor solutions on α-Fe cores synthesized above. Precursor volumes, addition routes, and temperatures were modified for multiple studies and solution were annealed for 30 min and an aliquot was removed for analysis. Synthesized NPs were oxidized by opening the reaction solution to air at 100 °C for 5 hours. NPs were precipitated with dry ethanol (~15 mL), followed by centrifugation (5 min, 4400 RPM). Final product was dispersed in hexane and stored under Ar in airtight bottles.

\(a\) Synthesis of α-Fe NPs: Crystalline α-Fe nanoparticles were then prepared via the thermal decomposition of Fe(CO)$_5$ in the presence of OAm, and HDACl.\textsuperscript{251,304} In a typical α-Fe synthesis, 19.0 mL of ODE, 200.0 mg HDACl, and 1.0 mL of OAm was combined and degassed at 120 °C for 1 h. This mixture was then heated to 180 °C in a four-neck flask under Ar. Then, 0.35 mL of Fe(CO)$_5$ was injected via a metallic Luer lock syringe into
the solution under Ar. The reaction mixture was agitated by bubbling Ar through the solution as well as by manual agitation, in order to limit α-Fe collection at a magnetic stir bar. After annealing for 30 minutes at 180 °C, half of the reaction volume was removed, cooled to room temperature, and then precipitated with dry EtOH. The un-cleaned α-Fe aliquots were kept in the reaction vessel under Ar gas and used as the core for nickel deposition, as described next. Shell precursor synthesis for Fe-Ni-Cr system: Cr precursor was prepared by dissolving 650 mg Cr(CO)$_6$ in 20 mL of dioctylether at 100 °C under inert atmosphere. 1.5 g of Nickel precursor Ni(CO)$_2$(PPh$_3$)$_2$ was dissolved in 20 mL THF under inert conditions at RT.

(b) Synthesis details for Fe/Ni/Cr NPs: Nickel Shell Deposition and Annealing at α-Fe cores:
Total of 9.4 mL Ni/THF solution was deposited to obtain theoretical thickness of 1 nm on previously synthesized α-Fe cores in layer-by-layer fashion, at 180 °C, under Ar blanket. Injection amount of Ni precursor was split equally in smaller volumes and added over 50 min to avoid dramatic temperature loss. Solution was annealed for 30 min at 180 °C.

Chromium Shell Deposition and Annealing at FeNi: 6.8 mL Cr precursor was added into solution of FeNi NPs under Ar at 180 °C in a layer-by-layer fashion. Solution was annealed for 30 min and aliquot was removed for analysis.

(c) Synthesis details for Fe/Cr/Ni NPs: Synthesis of Fe/Cr core/shell nanoparticles: In a typical synthesis,237 6.8 mL Cr precursor was added into solution of α-Fe NP cores (prepared as shown above) under Ar at 180 °C in a layer-by-layer fashion. For instance, a 2.3 mL aliquot was injected at each layer (n) to achieve theoretical Cr shell coating with shell thickness ~0.33 nm (providing complete dissolution of Cr precursor), then annealed for 15 min before additional shell depositions ($t_{S}= 0.33 - 1.0$ nm). The total annealing time
for a typical shell deposition is 60 min. ~2 mL aliquot was removed for analysis. *Nickel Shell Deposition and Annealing at Fe/Cr Core/Shell:* Total of 9.4 mL Ni/THF solution was deposited in layer-by-layer fashion at 180 °C under Ar blanket to obtain theoretical thickness of ~1 nm on the Fe/Cr core/shell material prepared as above. Injection amount of Ni precursor was split equally in smaller volumes and added over 50 min to avoid dramatic temperature loss. Solution was annealed for 45 min at 180 °C.

**(d)** Synthesis details for Fe/Cr$_x$Ni$_{1-x}$ alloy NPs: As prepared solutions of Ni(CO)$_2$(PPh$_3$)$_2$ in THF and Cr(CO)$_6$ in dioctylether were simultaneously injected into the hot solution of previously synthesized α-Fe cores in layer-by-layer fashion, at 180 °C under Ar blanket. Total injection volume of Ni- & Cr- precursors (5 mL each) was split equally in smaller volumes and added over 45 min to avoid dramatic temperature loss. After complete addition, solution was further annealed for 30 min at 180 °C, and aliquots were removed for analysis at various times. Annealing temperature was changed to 220 °C in next synthesis while maintaining all other parameters identical.

**(e)** Oxidation of the synthesized nanoparticles & Ligand Cleanup: The NPs synthesized above were oxidized by opening the un-cleaned reaction solution to air for 5 hours at 100 °C in an ODE oil bath. Particles were precipitated out with dry ethanol (~15 mL) addition followed by centrifugation (5 min, 4400 RPM). The precipitated NPs were re-dispersed in hexane and centrifuged again with additional ethanol. Final product was dispersed in hexane and stored under Ar in airtight bottles. CA-NPs were also heated at higher temperatures, essentially Fe/Cr$_x$Ni$_{1-x}$ NPs (0.5 mL, 14 mM) were added to a 25 mL round bottom flask containing10 mL ODE, 0.2 mL OAm and annealed in open air at 200 °C for 5 h. In next heating experiment, cleaned CA-NPs were dried and loaded on a zero
diffraction XRD substrate and were heated in an open-air oven at 150 °C for 24 h. NPs were also exposed to salt solution, where in CA-NPs were dropcast and dried on a silica substrate, which was then partly submerged in 5% NaCl solution for 48 h. Similarly, a metallic substrate was also spray-coated with Fe/Cr$_x$Ni$_{1-x}$ NPs and dipped to 5% NaCl solution for 10 days.

2.2.3. Instrumentation

All optical absorption data was acquired using a Varian Cary Bio100 UV-Visible Spectrophotometer (UV-Vis). TEM imaging was performed on a JEOL 2000EX instrument operated at 100 kV with a tungsten filament (SUNY-ESF, N.C. Brown Center for Ultrastructure Studies). Additional TEM imaging was performed on a JEOL JEM2100 microscope operated at 200 kV, with a LaB$_6$ electron source and CCD detector (Weiskotten Hall, Upstate Medical University, Syracuse, NY). Particle size and aspect ratio were analyzed manually, and statistical analysis was performed using either ImageJ or Corel Draw software on populations of at least 100 counts. Samples were drop cast onto a carbon coated copper grids. The powder X-ray diffraction (XRD) patterns were taken on a Bruker D8 Advance powder diffractometer using Cu-K$_\alpha$ radiation (1.5406 Å). The diffraction (Bragg) angles (2θ) were scanned over 20-80° at a step size of 0.04° with a scan speed of 20 sec/step. Samples were drop cast and dried on a zero-diffraction SiO$_2$ crystal (MTI Corp.). Estimate for the diffracting grains size was determined using Scherrer equation. X-ray Photoelectron Spectroscopy (XPS) measurements were performed on Surface Science Instruments (SSI) model SSX0100 that utilized monochromatic aluminum K-α X-rays (1486.6 eV) (Cornell Center for Materials Research, CCMR). The NP powders were dispersed on freshly cleaved Si substrates before analysis. The XPS analysis of peak binding energy and
deconvolution was performed using CasaXPS software, in which a Shirley background subtraction was used, as was a 50:50 Guassian:Lorentzian line widths. All XPS were corrected for charging using the standard C 1s peak position of 284.8 eV.

2.3. Results and Discussion

2.3.1. Effect of Shell Thickness & Role of Shell Deposition Order

The importance of shell deposition sequence and thickness was explored through the decomposition of Cr(CO)$_6$ or Ni(CO)$_2$(PPh$_3$)$_2$ at various molar ratios in the presence of $\alpha$-Fe NPs, under inert conditions. Figure 2.1 illustrates the synthesis of Fe/Ni/Cr and Fe/Cr/Ni CA-NPs by alternating Cr(CO)$_6$ and Ni(CO)$_2$(PPh$_3$)$_2$ decomposition sequence. We chose to study sequenced shell deposition in Ni and Cr rich compositions to allow us a way to drive alloying direction (core-to-shell, shell-to-core), and also to tailor oxidation of the NP. In order to promote alloying, and to produce nanomaterials with only a minimum shell, with overall thicknesses of 2 - 4 nm were chosen for best comparison. Here, the [Fe]:[Cr]:[Ni] molar ratios were such that each Cr or Ni addition resulted in $\sim$1 nm and $\sim$2 nm shell growth, which for simplicity we denote as thin and thick shell, respectively.
The addition of Cr(CO)$_6$ and Ni(CO)$_2$(PPh$_3$)$_2$ to a hot solution of α-Fe NPs is straightforward, however one major challenge faced was the low solubility of these precursors. We found that both precursors had very low solubility in preferred non-polar solvents such as octadecene (ODE) at RT and heating the Cr(CO)$_6$/ODE mixture only slightly improved the solubility. Precursor solubility improved dramatically in tetrahydrofuran (THF) but injecting this mixture to a solution containing α-Fe core NPs at high temperatures resulted in speedy evaporation of THF, accompanied by rapid heat loss. Finally, dioctylether (DOE) was found to be an optimal solvent with improved solubility at 100 °C. These precursor solutions were injected in a 4-neck flask containing previously synthesized α-Fe cores at slow addition rate (~0.5 mL/min) so as not to dramatically lower the reaction temperature. Any un-decomposed metal carbonyl stuck on the reaction flask wall was mixed back into the annealing solution by manually agitating the vessel. After completion of the deposition cycles and annealing, the NPs were split into two samples. The as-synthesized sample was purified and collect, whereas the second sample was opened to air and

Figure 2.1. A schematic showing the reaction routes towards the synthesis of α-Fe/Ni/Cr and α-Fe/Cr/Ni NPs via the sequenced thermal decomposition of Cr(CO)$_6$ and Ni(CO)$_2$(PPh$_3$)$_2$, with final reaction step oxidation at 100 °C. [Reproduced with permission from J. Phys. Chem. C, 2016, 120 (38), 22035–22044. Copyright © 2016 American Chemical Society.]
heated in a round-bottom flask at 100 °C for 5 h. This oxidized sample was then purified and collected. The synthesis was repeated a second time in which 2–3x more Cr(CO)\(_6\) and Ni(CO)\(_2\)(PPh\(_3\)) were added, resulting in thicker shells.

Figure 2.2. A schematic illustration of the Fe/Cr\(_x\)Ni\(_{1-x}\) NP synthesis via the simultaneous thermal decomposition of Cr(CO)\(_6\) and Ni(CO)\(_2\)(PPh\(_3\))\(_2\), at annealing temperatures of 180 and 220 °C.

We also synthesize Fe/Cr\(_x\)Ni\(_{1-x}\) core-alloy nanoparticles (CA-NPs) via similar the air free co-thermal decomposition deposition of Cr(CO)\(_6\) and Ni(CO)\(_2\)(PPh\(_3\))\(_2\) in the presence of highly crystalline α-Fe NPs, as illustrated in Figure 2.2. We recently introduced the core-alloy (CA) approach in metal and noble metal nanoparticles, and the aim is to alter particle growth and nano-performance by tailoring alloy phase behavior at a pre-synthesized interface, instead of attempting to make a homogeneous alloy. Herein, we focus on the potential of crafting a stainless-like nano-interface that would allow for the protecting of a metallic nano-core, which in this case is a metallic iron nanoparticle (α-Fe\(^{251,305}\)), from transforming into its oxide (i.e., Fe\(_3\)O\(_4\), Fe\(_2\)O\(_3\)). We then further explore the use of these CA-NPs as corrosion resistant thin-films. To this end, a precursor solution of Cr(CO)\(_6\) and Ni(CO)\(_2\)(PPh\(_3\))\(_2\) in which [Cr]:[Ni] ≈ 1 were dissolved in warm dioctylether and added to a solution of α-Fe core NPs maintained at 180 and 220 °C. The use these zerovalent precursors is important to overcome challenges presented by galvanic exchange with the interface if other precursors, like metal-acac are used.\(^{240}\) The Cr+Ni precursors are added in a slow manner.
(~0.5 mL/min), with each aliquot intended to form a sub-monolayer on the α-Fe seeds. This slow growth is important, and aids in uniform growth and alloying with the interface. Ultimately, this produces Fe/Cr\textsubscript{x}Ni\textsubscript{1-x}, where x \approx 0.5. The NPs were then either purified free of excess ligands by use of dry co-solvents, or first exposed to oxygen via the opening of the reaction vessel and heated at 100 °C (see section 2.2).

**Figure 2.3.** Representative TEM micrographs for thin shell Fe/Ni/Cr (a) and Fe/Cr/Ni (b) as-synthesized (i) and after oxidation in ODE opened to air at 100 °C for 5 h (ii). [Reproduced with permission from J. Phys. Chem. C, 2016, 120 (38), 22035–22044. Copyright © 2016 American Chemical Society.]
Transmission electron microscopy (TEM) was employed to investigate the morphology and microstructure of CA-NPs. Figure 2.3 shows the representative micrographs for the thin shell Fe/Ni/Cr (a) and Fe/Cr/Ni (b) CA-NPs for unoxidized (i) and oxidized NPs (ii). TEM for the Fe/Ni/Cr sample shows dispersed NPs along with few clusters and have relatively narrow size distribution with a diameter of $d_{C+S} = 10.6 \pm 2.6$ nm (Figure 2.3a-i). Upon air oxidation at elevated temperatures, these NPs show decreased circularity. Size increase to $12.3 \pm 3.3$ nm is confirmed by a wide size distribution shown in the inset (Figure 2.3a-ii). In the case of Fe/Cr/Ni NPs, TEM shows average NP diameter of $10.1 \pm 1.9$ nm (Figure 2.3b-i). It is expected that the outer nickel shell imparted moderate levels of contrast to slightly elongated NPs. After the oxidation step TEM shows scattered NPs, and the distribution is skewed towards higher size range with average diameter of $12.0 \pm 2.1$ nm (Figure 2.3b-ii). In general, deposition of 1 nm thin shells of Cr or Ni on $\alpha$-Fe cores does not significantly change the overall morphology of the CA-NPs. Minor variations in size distribution and oxidation induced size increase are typical features of these NPs. Interestingly, average shell thickness of the thin shell CA-NPs is revealed to be $\sim 2.1$ nm.
Figure 2.4. Representative TEM micrographs for thick shell Fe/Ni/Cr (a) and Fe/Cr/Ni (b) as-synthesized (i) and after oxidation in ODE opened to air at 100 °C for 5 h (ii). [Reproduced with permission from J. Phys. Chem. C, 2016, 120 (38), 22035–22044. Copyright © 2016 American Chemical Society.]

Looking at the thick shell CA-NPs, we find significantly different morphologies when transitioning from Fe/Ni/Cr (Figure 2.4a) to the Fe/Cr/Ni NPs (Figure 2.4b). In the first case, Fe/Ni/Cr NPs showed spherical nanoparticles with a diameter of $d_{C+S} = 10.9 \pm 2.2$ nm (Figure 2.4a-i). This size increase from 8 nm to ~11 nm is marginally less than the targeted $d_{C+S} = 12$ nm for a 4 nm thick shell. After the oxidation step, NP diameter increased to $15.4 \pm 3.3$ nm, which could be attributed to some broad clusters as shown by the size distribution graph (Figure 2.4a-ii). In contrast, the Fe/Cr/Ni NPs are much larger at $14.5 \pm 3.5$ nm and are faceted with high contrast.
islands (Figure 2.4b-i). On air oxidation, minor decrease in diameter is observed at 13.5 ± 2.5 nm, which is within the standard deviation limit. The TEM results are compared in table 2.1. We attribute some inconsistencies in the results to be related to the variation in the diameters of α-Fe NP cores used in each synthesis. For example, in the thin- and thick-shelled Fe/Ni/Cr both have similar diameters (~11 nm) but were built from ~2 nm smaller α-Fe NP cores in the thick-shell cases. New α-Fe were used in each synthesis, as opposed to one α-Fe NP for all due to the need to limit any premature oxidation of the cores that may have resulted due to storage or cleaning, which would limit alloying and metallic growth.

![Figure 2.5](image)

**Figure 2.5.** TEM micrographs for α-Fe core NPs (a) and Fe/Cr$_x$Ni$_{1-x}$ NPs synthesized at 220 °C (b).

Figure 2.5 shows a set of TEM micrographs for α-Fe cores and Fe/Cr$_x$Ni$_{1-x}$ CA-NPs collected immediately after synthesis at 220 °C. Compared to α-Fe core, which had a core diameter of $d_C = 8.3 \pm 1.2$ nm (a), the Fe/Cr$_x$Ni$_{1-x}$ CA-NP had an overall diameter of $d_{C+S} = 11.0 \pm 1.8$ nm (b). The NPs prepared at 180 °C also showed similar morphologies and diameters.
Table 2.1. TEM determined diameters ($d_{C+S}$) for as-synthesized and oxidized, thin and thick shell CA-NPs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thin Shell $d_{C+S}$ (nm)</th>
<th>Thick Shell $d_{C+S}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Ni/Cr (as-synthesized)</td>
<td>10.6 ± 2.3</td>
<td>10.9 ± 2.2</td>
</tr>
<tr>
<td>Fe/Ni/Cr (oxidized)</td>
<td>12.3 ± 3.3</td>
<td>15.4 ± 3.3</td>
</tr>
<tr>
<td>Fe/Cr/Ni (as-synthesized)</td>
<td>10.1 ± 1.9</td>
<td>14.5 ± 3.5</td>
</tr>
<tr>
<td>Fe/Cr/Ni (oxidized)</td>
<td>12.0 ± 2.1</td>
<td>13.5 ± 2.5</td>
</tr>
</tbody>
</table>

Figure 2.6. Powder XRD for thin (a) and thick shell (b) CA-NPs with composition of Fe/Ni/Cr (bottom panel) and Fe/Cr/Ni (top panel). The as-synthesized (red) are compared with oxidized (blue). Reference reflections Fe, Cr, Ni, Fe$_3$O$_4$, FeCr$_2$O$_4$, and NiFe$_2$O$_4$ are shown for comparison. [Reproduced with permission from J. Phys. Chem. C, 2016, 120 (38), 22035–22044. Copyright © 2016 American Chemical Society.]
Powder X-ray diffraction (XRD) was employed to understand the crystal structure, oxidation, and alloying of CA-NPs. Figure 2.6 shows the XRD results for thin (a) and thick shell (b), Fe/Ni/Cr (i, ii) and Fe/Cr/Ni (iii, iv) NPs. Several important observations can be drawn from the XRD results. Firstly, all of the samples show retention of metallic reflections to a certain extent (b.c.c. Fe/Cr<sub>110</sub> at ~44.4°). Secondly, it is clear that the extent of oxidation is highly sensitive to both shell deposition sequence and thickness.

Thin shell Fe/Ni/Cr NPs experienced increased oxidation as evidenced by the presence of strong <311> & <220> reflections corresponding to M₁O₄ (M = Fe, Ni, Cr). XRD patterns for both as-synthesized and oxidized samples do not change significantly indicating rapid oxidation of these NPs, which is anticipated due to oxidation prone external Cr shell (Fig. 2.6a-i, -ii). Absence of a Ni <200> reflection (see standards in inset) is rationalized due to the layer adapting a b.c.c. at low coverage (i.e., low compositions), as observed previously in thin film studies. Interestingly, as the shell sequence is reversed, strong metallic b.c.c. Fe/Cr <100> and f.c.c Ni <111> reflections are observed without any corresponding f.c.c <200> reflections, and with little to no <311> oxide reflections, either before or after oxidation (Fig. 2.6a-iii, -iv). The thin outer layer of Ni is again hypothesized to have adapted a b.c.c. structure, but this time can undergo strain relaxation at the NP surface, aiding in oxidation resistance (see below).

For thick shell Fe/Ni/Cr NPs (Figure 2.6b-i, ii) the prominent feature of the XRD is the <110> reflection associated with the b.c.c. α-Fe core. Intense <311> reflections, as seen in thin shell counterpart are not seen, however minor M₁O₄ oxide growth (M = Fe, Ni, Cr) is observed. These observed improvements in oxidation resistance with shell growth follows the expected trend. Appearance of f.c.c. Ni<sub>200</sub> reflection is likely due to the NP transitioning to a more Ni-rich periphery (see below). However, for thick shell Fe/Cr/Ni NPs, a much larger M₁O₄ signal is
observed, which further intensifies after the oxidation step (Figure 2.6b- iii, -iv). Apparent peak broadening after the oxidation step at ~44.2°, is in fact is due to the merging of metallic <110> with metal oxide <400> reflection, which incidentally appears at 43°. As indicated in corresponding TEM images, it is expected that nickel does not form a symmetric shell at higher shell thicknesses, possibly inducing fast diffusion pathways.

**Figure 2.7.** Compared are the powder XRD patterns of Fe/Cr\textsubscript{x}Ni\textsubscript{1-x} NPs synthesized at 180 °C (a-d, i) and 220 °C (a-c, ii). XRD of Fe/Cr\textsubscript{x}Ni\textsubscript{1-x} CA-NPs as-synthesized (a), upon solution heating in ODE open to air at 100 °C for 5 h (b), thin-film heating in air at 150 °C for 24h (c), and thin-film heating in air at 200 °C for...
5h (d). Representative XRD patterns for unoxidized α-Fe cores (e, i) that after complete oxidation form Fe$_3$O$_4$ NPs (e, ii). Comparison of the reflections associated with the metal oxides (M$_3$O$_4$, <311>) and metallic Ni (f.c.c. <200>) relative to the metallic peak at ~44.4° for Fe/NiCr NPs synthesized at 180 °C (f) and 220 °C (g). Note that for pure Ni, the ratio of <200>/<111> is ~0.41, which is only reached with annealing at 200 °C for 5 hours in (f).

Next, the ability of the Fe/Cr$_x$Ni$_{1-x}$ to resist oxidation was characterized by powder X-ray diffraction (XRD). Figure 2.7 shows a series of XRD that compares CA-NPs prepared at 180 and 220 °C. A major characteristic of each is the metallic nature of the NP. For example, (a) shows the as-synthesized NPs (i, ii) which reveal metallic <110> and <111> reflections at ~44.4° that correspond to the inner α-Fe (b.c.c.) and peripheral γ-Ni, γ-FeCrNi (f.c.c.) characteristics of the NP (see chapter 3), respectively; the latter of which is associated with rich Ni compositions. Of importance is the lack of oxide reflections, as only minor oxide (M$_3$O$_4$, M= Fe, Cr, Ni) <311> reflections are observed at 2θ of ~35.5°, indicating low oxide content, especially for the Fe/Cr$_x$Ni$_{1-x}$ prepared at 220 °C. When the Fe/Cr$_x$Ni$_{1-x}$ NPs were heated in the vessel at 100 °C open to air (b) little change is observed in the XRD with oxide growth below the detection limits of the measurement.

Interestingly, similar performance was observed when the CA-NPs were dried as thin films and heated at 150 °C for 24 h and 200 °C for 5 h, as shown in Figure 2.7(c) and 2.7(d), respectively. In each case only a minor growth of the <311> reflection is observed. In addition, the fwhm of the primary <111> reflection does not decrease considerably, indicating that in addition to oxidation resistance, the NPs also resist agglomeration well. These XRD characteristics are in contrast to typical transition metal nanoparticles, which are either synthesized in the oxide form, or become readily oxidized after synthesis (e.g. TiO$_2$, SPIONs). For example, a control experiment is shown in Figure 2.7(e), where α-Fe NPs, capped with similar HDACl and OAm ligands, underwent similar oxidation while in ODE solution at 100 °C for 5h. While metallic after synthesis (i), the
NPs completely transforms into Fe$_3$O$_4$ spinel structures as a result of the oxidation (ii), which further reinforces the stainless qualities of the CrNi layer in this study. Finally, to qualitatively compare oxidation in, the $<311>/<111>$ (in red) and $<200>/<111>$ intensity ratios (in blue) were plotted for CA-NPs synthesized at 180 °C and 220 °C, in Figure 2.7(f) and 2.7(g), respectively.

To obtain the shell composition and surface layer oxidation details, the NPs were characterized by X-ray photoelectron spectroscopy (XPS). For simplicity, we focus on the thin-shell CA-NPs. Table 2.2 shows the metal composition before and after oxidation. The XPS composition table for Fe/Cr/Ni and Fe/Ni/Cr NPs shows fluctuations in Fe composition between ~19-42%, which is likely due to the varying thickness of the Ni-Cr shells (2.3 and 1.8 nm, respectively) which leads to higher signal contribution from the core. After oxidation, both Fe/Ni/Cr and Fe/Cr/Ni CA NPs show a Fe composition of ~35% reflecting a steady migration of Fe into the growing oxide. Nickel shows higher % composition as compared to Cr, but in both cases Ni content decreases after the oxidation step by ~20%, indicating lower content of Ni in the outer oxide layer. As seen in Figure 2.8(c), Cr 2p region is rapidly oxidized, which hinders the precise determination of Cr wt%.
The CA-NP samples were further investigated via XPS to obtain the binding energy (B.E.) peak data for comprising metals. Figure 2.8 shows a collection of XPS results for the 2p region of Fe, Cr, and Ni for Fe/Ni/Cr (a, b, c), and Fe/Cr/Ni NPs (d, e, f). In each case data for both as-synthesized (i) and oxidized (ii) samples are shown.

For Fe/Ni/Cr NPs, Fe core diffusion through an already oxidized Cr shell allows formation of FeCr$_2$O$_4$/NiFe$_2$O$_4$ metal oxide species\textsuperscript{306}, indicated by B.E. of $\sim$711.7 eV (Figure 2.8a). Nickel initially showed singular metallic peaks, but after oxidation, improved intensity reveals multiple peaks corresponding to NiO, NiO.M$_2$O$_3$ (M= Fe, Cr) along with metallic Ni (Figure 2.8b-ii).\textsuperscript{306–308} It is possible that zerovalent Ni is the reduced product in galvanic exchange between partially...
oxidized Ni and Cr species. High B.E. of 581.3 eV showed presence of Cr (VI) oxide before oxidation, but oxidation heating led to core diffusion, forming mixed metal oxides FeCr$_2$O$_4$, NiCr$_2$O$_4$ (Figure 2.8c).$^{306,309}$

In the case of Fe/Cr/Ni NPs, XPS analysis of unoxidized sample shows Fe 2p(3/2) peak at 712.4 eV, establishing presence of Fe$_3$O$_4$/FeCr$_2$O$_4$ metal oxide. After the intentional oxidation step, a slight shift to higher B.E. indicates formation of intermediate mixed oxides Fe$_3$O$_4$/Fe$_2$O$_3$ (Figure 2.8d-i, ii).$^{306,310,311}$ Nickel initially appears as Ni$^0$, but showed formation of oxide species as indicated by minor B.E. shift to 856.3 eV (Figure 2.8e-ii). XPS analysis for Cr 2p peaks indicated formation of Cr$_2$O$_3$/CrO$_3$ with peaks at 576.6 eV & 579.2 eV, which after oxidation showed a single broad B.E. peak corresponding to NiCr$_2$O$_4$/FeCr$_2$O$_4$ (Figure 2.8f). It is expected that Ni and Cr form a stable M$_3$O$_4$ (M = Cr, Ni) species at the surface.$^{309}$

A closer look at the chromium XPS spectra region for both the CA-NPs show that with an average B.E. shift of 4.48 eV, Cr 2p(3/2) peaks have almost always shifted to a higher binding energy, indicating rapid chromium oxidation. This is not surprising considering that chromium has the lowest reduction potential among these three metals (Cr$^{2+}$ < Fe$^{2+}$/Fe$^{3+}$ < Ni$^{2+}$).$^{308}$ Presence of thinner shells may have contributed towards core diffusion to form Fe$_3$O$_7$ surface layer, yielding broader Fe 2p peaks. Nickel on the other hand has shown promising potential for oxidation tolerance with an average B.E. shift of 1.44 eV, lowest among the three. Even though minor shifts in Ni 2p peak are observed after the oxidation step (Figure 2.8b-ii), they co-exist along with the standard metallic B.E. peaks, confirming the contribution of Ni shell towards oxidation resistance properties.
Figure 2.9 XPS for the 2p Binding Energy regions of Ni (a), Fe (b), and Cr (c) are shown for Fe/Cr$_x$Ni$_{1-x}$ NPs, before (i, red) and after the intentional oxidation step (ii, green). Binding energy values for unoxidized and oxidized samples are tabulated as well.

Table 2.2 shows that the XPS determined atomic composition of Fe/Cr$_x$Ni$_{1-x}$ CA-NPs before oxidation was 43.1% Ni, 37.6% Fe, and 19.3% Cr. Oxidation step did not induce major compositional changes; only a minor increase in Ni composition is observed, suggesting inward shell-to-core diffusion. Deconvoluting binding energy peak revealed presence of metal oxide species at the interfaces. In Figure 2.9a(i), before oxidation Ni 2p$_{3/2}$ peak showed a good match with metallic Ni binding energy (BE), however after the oxidation step minor BE shift to higher value is observed, indicating presence of nickel oxide species. Figure 2.9b(i) shows the Fe 2p$_{3/2}$
peak with minor peak at 704.4 eV and a more prominent peak at 711.8 eV. Alloying at the shell interface prompts differential charging, which in turn may yield higher $fwhm$ as seen in the broader Fe$_{3/2}$ peak. Formation of multiple peaks after oxidation indicates presence of several mixed oxide species including FeCr$_2$O$_4$, NiFe$_2$O$_4$, and Fe$_2$O$_3$.\textsuperscript{306,307,312} As shown in Figure 2.9(c), Cr is oxidizes readily due to its comparatively lower reduction potential and shifts to higher BE with relatively wider peak.

**Table 2.2.** XPS determined composition for Fe/FeCrNi CA-NPs.

<table>
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<tr>
<th>Sample</th>
<th>As synthesized Composition (%)</th>
<th>Oxidized Composition (%)</th>
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<tbody>
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<td></td>
<td>Fe</td>
<td>Ni</td>
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<tr>
<td>Fe/Ni/Cr</td>
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</tr>
<tr>
<td>Fe/Cr$<em>x$Ni$</em>{1-x}$</td>
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<td>43.11</td>
</tr>
</tbody>
</table>

**Table 2.3.** XPS binding energy (B.E. in eV) values for un-oxidized thin-shell CA-NPs:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fe (2p)</th>
<th>Ni (2p)</th>
<th>Cr (2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/2</td>
<td>3/2</td>
<td>1/2</td>
</tr>
<tr>
<td>Fe/Ni/Cr</td>
<td>730.12</td>
<td>711.7, 716.8 (sat.)</td>
<td>877.74</td>
</tr>
<tr>
<td>Fe/Cr/Ni</td>
<td>726.64</td>
<td>712.4</td>
<td>875.56</td>
</tr>
<tr>
<td>Fe/Cr$<em>x$Ni$</em>{1-x}$</td>
<td>722.55</td>
<td>704.46, 711.81</td>
<td>872.75, 880.25</td>
</tr>
</tbody>
</table>

**Table 2.4.** XPS binding energy (B.E. in eV) values for the oxidized thin-shell CA-NPs:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fe (2p)</th>
<th>Ni (2p)</th>
<th>Cr (2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/2</td>
<td>3/2</td>
<td>1/2</td>
</tr>
<tr>
<td>Fe/Ni/Cr</td>
<td>725.61, 732.33</td>
<td>706.4, 711.8</td>
<td>873.36, 880.23</td>
</tr>
<tr>
<td>Fe/Cr/Ni</td>
<td>725.69</td>
<td>711.1, 711.9, 714.8</td>
<td>874.71, 880.65</td>
</tr>
</tbody>
</table>
2.3.2. Discovery of \( \sigma \)-phase in nanoscale Fe-Cr-Ni alloy

![Diagram of XRD pattern and ternary alloy phase diagram]

Figure 2.10. Powder XRD shows the presence of \( \sigma \)-phase in Fe/Cr\(_{1-x}\) Ni\(_x\) NPs when synthesized at elevated synthesis temperatures of 250 °C. This phase has previously not been observed in the nanoscale Fe-Cr-Ni alloys. Metallic peaks for \( \alpha \)-phase do not match with \( \sigma \)-phase peaks, and this absence of overlapping peaks confirms new alloy phase. Minor oxide peak also seen at \( 2\theta \approx 35.5, 63.5^\circ \) indicate possible oxidation before complete phase transformation. Ternary alloy phase diagram at 900 °C for bulk stainless steel containing iron, chromium, and nickel is shown. (Reproduced from the ASM Handbook of Alloy Phase Diagrams)

CA-NPs showed complete transformation from the alpha (\( \alpha \)) to a rare sigma (\( \sigma \)) phase when synthesized at even higher temperatures (>250 °C). This phase behavior was first reported in 1927 for bulk alloys,\(^{314}\) but has never been reported in nanoscale Fe-Cr-Ni alloys. Figure 2.10 show the powder XRD pattern for \( \sigma \)-Fe/Cr\(_{1-x}\)Ni\(_x\) where in \(<112>\), \(<411>\) reflections match well with \( \sigma \)-CrFe alloy with a tetragonal lattice. Bulk phase diagram for Fe-Cr-Ni ternary alloy indicates irreversible transition to the \( \sigma \) phase at higher Cr compositions of ~30-50%.\(^{314}\) It is expected that high annealing temperature during the synthesis led to recrystallization and faster atomic movement forming a
thermodynamic product with concentrated Cr-rich shell. Bulk scale σ-phase steels typically are hard, have low ductility, show lower corrosion resistance and are non-magnetizable. At the nano-scale the alloying temperatures are lowered and thus the phase diagram for NPs synthesized at ~200 °C is comparable to the bulk phase diagram at 900 °C. XPS determined compositions place the Fe/Cr$_x$Ni$_{1-x}$ NPs (synthesized at 180 and 220 °C) in the 18-8 stainless steel region. 18-8 steel, also known as SAE 304 and A2 Stainless steel, has excellent corrosion resistance (improved corrosion resistance over 400 series) and is widely used for manufacturing household utensils as well as industrial structures. These are austenitic steels and show weak magnetism. Increasing the synthesis temperature may lead to faster atomic movement in Cr shell and thus forming Cr-aggregates, resulting in the formation of σ phase as demonstrated in the phase diagram.

2.3.3. Salt Solution Stability of Fe/Cr$_x$Ni$_{1-x}$ CA-NP

![Figure 2.11](image.png)

Figure 2.11. Schematic illustration of the Fe/Cr$_x$Ni$_{1-x}$ NP synthesis (a), and oxidizing conditions as colloids in solution (b), dried powder at elevated temperatures (c), and as thin-films submerged in salt-water (d). XRD of Fe/Cr$_x$Ni$_{1-x}$ as-synthesized at 220 °C (i), and after exposure to a 5% NaCl solution for 48 h (ii). Inset: Image of XRD thin-film under exposure.
With this performance understood we next studied how the Fe/Cr$_x$Ni$_{1-x}$ react when exposed to a salt-rich environment. The Fe/Cr$_x$Ni$_{1-x}$ were dried as a thin-film and submerged in a in 5% (w/v) NaCl solution for 48 h. Figure 2.11 shows the XRD before (i) and after this exposure (ii). Remarkably, the Fe/Cr$_x$Ni$_{1-x}$ NPs withstood this corrosive environment, with only a minor <311> reflection is in the XRD results. Additional studies have revealed that the NPs can withstand such an environment for at least 9 months. Taken together these results demonstrate that the alloy nature of the NPs interface can protect the NP from oxidation both at high temperatures as well as corrosive environments. We hypothesized that such a NP would be good at protecting a metal surface from oxidation. With this in mind, we developed a simple spray coating technique where the Fe/Cr$_x$Ni$_{1-x}$ were dispersed in hexane at high concentrations (~15 mM) and used as ink in spray-paint like setup. We then deposited a ~5 mm thin film onto a metallic substrate and followed oxidation by eye over multiple months. Figure 2.12 depicts this control experiment where time-lapse images of the uncoated (a) and Fe/Cr$_x$Ni$_{1-x}$ coated (b) substrates are shown. Within 6 days the control substrate started showing formation of rust around the corners (a), while the coated substrate showed no change from the initial position (b). After 10 days (c), much higher amount of rust is concentrated on top of the control substrate, and still no rust is visible on the surface of NP coated substrate (d). Minor coating wear is seen at the bottom of the ring, which is entirely preventable with aid of a polymeric binder. Magnetic nature of the substrate (commercial NdBFe ring magnets) may have improved binding of magnetic NPs.
2.3.4. Theoretical Assessment of Diffusion and Oxidation in Fe/FeCrNi CA-NPs

The improved stainless character of the CA-NPs is due to the formation of an inert oxide layer at the nanoparticle surface according to the Cabrera-Mott theory.\textsuperscript{317,318} When considering alloy oxidation, heat of formation for the different oxides, oxidation rates, the inherent relative solubility of each oxide, and metal diffusion in the alloy are critical.\textsuperscript{319} While all three of the metals will readily oxidize,\textsuperscript{320} Cr is highly favored for oxidation relative to Ni, with Cr forming the passivation layer fastest. Moreover, as both NiO and Cr\textsubscript{2}O\textsubscript{3} are efficient inhibitors of oxygen diffusion, both metals provide stainless character to the Fe NP core.
Figure 2.13: Qualitative assessment of the oxidation resistance (a) of the different morphologies for thin (2 nm) and thick (4 nm) shell architectures using the ratio of the <311> $\text{M}_3\text{O}_4$ reflections to metallic <110> (and <111>) reflections. Analysis of the oxidation rates of each of the metals (b) shows that Fe and Cr oxidize much faster than Ni. Inset: The same computations under identical field strength conditions. Oxidation induced diffusion profiles from the center of the NP to the surface (c) are shown both for Fe/Cr/Ni (i) and Fe/Ni/Cr (ii) using bulk values extrapolated to 100 °C. [Reproduced with permission from J. Phys. Chem. C, 2016, 120 (38), 22035–22044. Copyright © 2016 American Chemical Society.]

Taken together, it is clear that shell type and sequence plays a major role in the CA-NP composition and microstructure, resulting in different oxidation characteristics. To better understand this, we again consider the XRD results from Figure 2.6 and compare the results by plotting the ratio of the <311> to <110> reflection intensity ratios, shown in Figure 2.13(a). Here,
a higher value indicates higher degrees of oxidation, and the results are compared for thin-shell (denoted as 2 nm), and thick-shell (denoted as 4 nm). By comparing before and after oxidation (gray vs. red bars), it becomes clear that the thin-shell samples have the most oxidation resistance, and further that Fe/Cr/Ni performs better than Fe/Ni/Cr. To better understand this trend, we next compare these results based on assessments of alloying, diffusivity, and oxidation rates, as well as the potential relationship of shell order to crystal strain.

To rationalize how shell sequence affects NP oxidation, we approximated how iron, nickel and chromium alloy at temperatures of ~500 °C. We chose this temperature, as opposed to our synthesis temperature (180 °C) as a way to approximate the nano interface, considering that the metal surfaces of such nanoparticles melt at depressed temperatures, and because the phase behavior of metals at this low temperature are well known. From alloy phase diagrams, it is observed that chromium has higher miscibility (9%) with the α-Fe than nickel (5%), and it has an even higher solubility in f.c.c. nickel (22%). In contrast, nickel solubility is low in b.c.c. chromium (3%). Further, recent calculations for the nanoscale particles have predicted favorable mixing enthalpy for each binary couple of iron, nickel, and chromium (with the highest free energy coming from the mixing of chromium and nickel), further suggesting likelihood of alloying. This is further reinforced by thin-film studies for Fe-Cr, Ni-Fe, and Ni-Cr thin films, each of which showed favorable alloying tendency. Enhanced doping of the Cr-layer into f.c.c. Ni results in a much better alloy, whereas the alloying of Ni into the b.c.c. Cr-layer is poor, likely resulting in phase segregation (i.e., precipitation) leading to enhanced strain and cracks, and poor oxidation resistance. This phase segregation would be the most pronounced in the thick shell systems, which are less likely to alloy. This is reinforced in the data where the thin shell systems show little f.c.c. (Ni<111>), likely due to Ni-layer alloying and adopting a b.c.c. lattice as observed. A b.c.c. CrNi
structure has been observed both experimentally\textsuperscript{329,330} and computationally\textsuperscript{331}. In addition to phase behavior, we also considered what role of the surface energy ($\gamma$)\textsuperscript{325} and the relative diffusion constants might play in our systems. For example, $\gamma_{\text{Cr}}$ is the lowest (2.300 J/m$^2$), followed by $\gamma_{\text{Ni}}$ (2.450 J/m$^2$) and $\gamma_{\text{Fe}}$ (2.475 J/m$^2$),\textsuperscript{332} which implies that Cr prefers to rest at the interface, as has been observed in both bulk stainless steels\textsuperscript{333} and in Ni-Cr alloy NPs.\textsuperscript{334} However, several examples of phase segregation in homogenous alloy nanoparticles\textsuperscript{334,335} and alloying of core-shell NPs\textsuperscript{336,337} show that high temperature is needed to induce efficient transformations. Even taking into account that diffusion at the nanoscale can be orders of magnitude faster,\textsuperscript{338,339} our results suggest only alloying at the shell periphery or at the interface of the layers; were we to observe complete alloying, no difference in oxidation resistance as a function of shell sequence would be discerned. It is important to note that the $\Delta G$ gained from oxidation is the most for Cr, followed by Fe and then Ni,\textsuperscript{320} which is congruent to the sequence of relative metallic character retention observed experimentally via XPS in this system (Figure 2.9).

These alloying and diffusion characteristics are pertinent to our system as the synthesis is performed with zerovalent (i.e., metallic) precursors under inert conditions at elevated temperatures. However, if an oxygen source is present, or after the planned oxidation step (i.e., heating open to air, dried films), then oxidation behavior, and atom diffusion in or around that oxide is also required. Oxidation rates in metals and metallic thin films are classically treated with Cabrera-Mott (CM) theory,\textsuperscript{317} with further refinements to include coupled currents\textsuperscript{340} and the nature of the ionic conduction within the oxide.\textsuperscript{318} Application of this theory to nanomaterials has been undertaken by others,\textsuperscript{258} although the nanoscale provides further intricacies such as strain influenced diffusion,\textsuperscript{341} facet dependent oxidation,\textsuperscript{342} and 3-D boundary conditions.\textsuperscript{343} It is important to note that application of CM theory quantitatively to nanomaterials is still
problematic. Nevertheless, the underlying mechanism provides a good qualitative framework for approaching oxidation in mixed metal systems, and we applied CM theory to obtain oxidation rates in an idealized system to compare with our experimental results by using following equation 1:

\[
\frac{dX}{dt} = N \Omega v e^{-(W - qaV_M) / (kT)}
\]

where \(N\) is the number of potentially moving ions, \(\Omega\) is the volume of oxide formed per metal ion, \(v\) is the frequency of ionic motion, \(W\) is the activation energy for diffusion, \(q\) is the net charge of the moving ion given by \(Ze\), \(2a\) is the ion jump distance, \(V_M\) is the Mott potential, \(x\) is the thickness of the oxide layer, \(k\) is the Boltzmann constant, and \(T\) is the temperature. Here, \(V_M\) is dependent on the Fermi level of the oxidizing metal and the oxide species formed at the surface, which generates an electric field \(E = V_M / x\). Notably, while \(\Omega, 2a, v\) can be obtained from analysis of the lattice and bulk materials, caution must be used when utilizing \textit{a priori} values of \(W, N, V_M\), as these can be quite difficult to ascertain at the nanoscale (see supporting information for further discussion). As a first approximation, we use the values of given by Fehlner in fitting the thin film oxidations of Ni, Fe, and Cr with a constant \(V_M\).

Figure 2.13b shows the calculated oxidation profiles with a fixed \(V_M\) (inset, \(V_M = 2.4\) V) and for varying \(V_M\)'s (main panel, \(V_M = 1.6\) for Fe, 1 for Ni, and 2.1 V for Cr) ascertained from work-function changes of thin films during oxidation. In both cases, Fe and Cr have similar, rapid, oxidation whereas Ni oxidizes slower and terminates earlier (i.e. when \(dx/dt \leq 10^{-5} \text{ Å/s}\)). Once this oxide layer has been formed, metallic diffusivity is varied as compared to the simple phase characteristics described above. Figure 2.13(c) shows the relative diffusion couples of the Fe/Cr/Ni and Fe/Ni/Cr architectures. These values are based on extrapolation of bulk measurements to 100 °C (please see tables in supporting info in ref\textsuperscript{238}), and are approximations.
considering that diffusion inside a nanocrystal can be several orders of magnitude faster than bulk. For example, shown in Figure 2.13(c) is how both NiO and Cr$_2$O$_3$ strongly inhibit the diffusion of oxygen ions (O$^{2-}$), but both freely allow metal diffusion through to the NP surface. Interestingly, the values suggest that Cr atoms diffusion rapidly through both Ni and NiO but are essentially stationary in Cr$_2$O$_3$. Considering the XPS results (Fig. 2.9), this suggests that Cr may be the first metal to be oxidized either at the surface (as in the Fe/Ni/Cr architecture) or through rapid diffusion through the shell (as in the Fe/Cr/Ni architecture). Studies of Cr diffusion have found it to be the fast diffuser in Fe-Ni-Cr alloys as well as from modeling of Fe-Cr and Ni-Cr binary couples, supporting this hypothesis. The importance of Cr in the shell sequence may also be to slow Fe diffusion from the $\alpha$-Fe core, relative to the same process in Ni. In the thin shell systems, for example, we observe the best stainless character in Fe/Cr/Ni compared to Fe/Ni/Cr. This phenomena may be similar to that found in electronics components where Cr layers have been shown to reduce Au diffusion from metal contacts into the light absorbing layers of solar cells. It is also noteworthy that both of these systems do not show hollow, yolk–shell, or core-void-shell morphologies, further suggesting that Fe is trapped in the core.
With these experimental results and insights from classical theory in hand, we present a proposed mechanism for the core/alloy system in Figure 2.14. The experiments revealed that thin shells show enhanced oxidation resistance (a and c) relative to thick shells (b and d), and that stainless character is highly dependent on the shell deposition sequence. The thin Fe/Cr/Ni NP (a) showed the best resistance, which we hypothesize is largely due to the good epitaxial growth and alloying of Cr on α-Fe, followed by pseudo-epitaxial growth and alloying of Ni, and subsequent lattice relaxation at the interface. In contrast, the thick Fe/Cr/Ni (b), showed significant oxidation which can be rationalized due to poorer alloying of the thick layers, which would result in significant strain at the Cr-Ni interface (b.c.c.-f.c.c.) due to poor miscibility. These strains would likely lead to defects which would diminish oxidation resistance, a hypothesis which will be

Figure 2.14. Mechanistic summary of the behavior/properties observed in Fe/Cr/Ni (a, b) and Fe/Ni/Cr (c, d) in both the thin (left) and thick shell regimes (right). [Reproduced with permission from J. Phys. Chem. C, 2016, 120 (38), 22035–22044. Copyright © 2016 American Chemical Society.]
explored further in future work. When reversing the shell order, the thin-shelled Fe/Ni/Cr (c) retains some oxidation resistance but markedly less than when Cr is the middle layer. We again attribute this to improved alloying and more complete shell growth as described above in (a). Finally, thick-shelled Fe/Ni/Cr (d) also shows oxidation, albeit better than (b), which we attribute to less strain and defect formation like in (b) in the shell layer, and on higher Cr oxidation rates with reduced Fe diffusion through the intermediate Ni layer. Considering the resolution of the microscopy employed in this study, more work is needed to fully confirm this hypothesis by studying the precise interfacial composition of each nanoparticle, possible variations between particles, extent of alloying, and defect related oxide growth. In addition, many more variations in the core-alloy design can be implemented in order to even more fully protect the ferromagnetic cores from oxidation which may lead to new performance gains in magnetism, conductivity, and applications in corrosion resistant coatings, each of which is part of our ongoing work.

For the Fe/Cr$_x$Ni$_{1-x}$ CA-NPs, TEM in Figure 2.5 show no change in contrast from the core to the CA-NPs, suggesting relatively un-oxidized NPs. Powder XRD patterns in Figure 2.7 indicate high metallic character, the generated oxide layer must be fully encompassing the particle with only minor diffusion of the core to the NP periphery. The importance of crystal structure and intermetallic diffusion is further illustrated in Figure 2.7(c), where the nanoparticles synthesized at 180 °C were further annealed at 200 °C for 5 h to see if increased temperature led to increasing oxidation. No increase in oxide signature was seen. Intentional alloying likely reduces interfacial strain in the core-shell architecture (leading to better shell coverage), while simultaneously improving metallic diffusion in the shell (as has been shown for Cr diffusion in f.c.c. Ni$^{350,351}$) which accelerates the formation of the passivation layer.
2.4. Conclusion

In summary, the synthesis of transition metal core/alloy nanoparticles was described and theoretical analysis of oxidation and diffusion trends in the systems was provided. Fe/Ni/Cr, Fe/Cr/Ni, and Fe/Cr\textsubscript{x}Ni\textsubscript{1-x} CA-NPs were synthesized in either thin- or thick-shell variations via the thermal decomposition of Cr(CO)\textsubscript{6} and Ni(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} at α-Fe cores. TEM analysis showed NP growth, whereas the oxidation properties observed via powder XRD, and XPS provided insight into composition and oxidations states. In addition to the new synthetic route, the primary finding of this work is that thin shells exhibit better oxidation resistance (i.e. stainless character) compared to thick shells, the extent to which is also defined by shell deposition sequence. These observations were considered by comparison to bulk alloy miscibility and phase behavior, crystal structure, oxidation rates, and metallic diffusion. This work demonstrates the potential of constructing transition metal nanoparticles that retain metallic characters, which may pave the way for performance gains in nano magnetism and conductivity, which in turn could lead to new forms of stainless thin-films, magnetic coatings, and long lasting nano properties.
Chapter 3

Oxidation and the Voids Formation in Fe<sub>x</sub>Cr<sub>1-x</sub> Alloy Nanocubes

In this chapter I describe the synthesis of cube-shaped Fe<sub>x</sub>Cr<sub>1-x</sub> alloy NPs and high resolution TEM study of oxidation and internal void formation in these NPs. These alloy NPs were subjected to oxidation at various temperatures and effect of annealing on the subsequent formation of internal voids was studied. Formation of Fe<sub>x</sub>Cr<sub>1-x</sub> alloy nanocubes is described, and better understanding of the extent of oxidation and diffusion is obtained from atomic resolution images. Results show that the extent of oxidation and internal void formation in the Fe<sub>x</sub>Cr<sub>1-x</sub> nanocubes is highly dependent on oxidation environment.

3.1. Introduction

Oxidation in nanomaterials is a general approach to control shape and morphology of nanoparticles, and especially, the oxidative Kirkendall diffusion is often preferred protocol for synthesizing nanoparticles with internal voids. This process exploits the relative difference in the oxidation rates of alloying component, and works very well in the case of core/shell nanomaterials. In our previous work describing the oxidation in binary transition metal core/shell systems, formation of hollow Fe/Fe<sub>x</sub>Cr<sub>1-x</sub>, Fe/Fe<sub>x</sub>Ni<sub>1-x</sub> nanoparticles has been shown. For example, in Fe/Fe<sub>x</sub>Ni<sub>1-x</sub> core/shell NPs, oxidation and subsequent outward diffusion of Fe core leads to formation of hollow NiFe<sub>2</sub>O<sub>4</sub> NPs.

In case of core/shell nanoparticles, the typical result of oxidative diffusion is either complete hollowing of the core (e.g. hollow Fe<sub>3</sub>O<sub>4</sub> NPs) or incomplete oxidation resulting in core/void/shell morphologies. However, this hollowing is not so predictable in case of non-
spherical, alloyed nanoparticles. Depending on the lattice parameter and packing type of the components, metallic alloy NPs may exhibit highly miscibility (e.g. Au-Ag NPs\textsuperscript{65}) or on the other hand, might form heterostructured nanoparticles (e.g. Pt-Fe NPs\textsuperscript{161,356}). Along with this dependence, non-spherical morphology often results in lack of symmetric diffusion channel in alloys NPs\textsuperscript{357}.

![Figure 3.1](image)

**Figure 3.1.** Schematic shows the synthesis of the Fe\textsubscript{x}Cr\textsubscript{1-x} alloy via simultaneous decomposition of Fe(CO)\textsubscript{5} and Cr(CO)\textsubscript{6} in presence of HDACl, oleylamine and octadecene. Subsequent oxidation procedure and final product morphologies with internal voids are depicted.

In this work, I study the oxidative diffusion in cube-shaped Fe-Cr alloy nanoparticles. This study focuses on the morphological evolution of the Fe\textsubscript{x}Cr\textsubscript{1-x} nanocubes as a function of oxidation temperature. Figure 3.1 shows that the Fe\textsubscript{x}Cr\textsubscript{1-x} alloy NPs were synthesized using simultaneous decomposition of metal carbonyl precursors the high temperature in presence of organic ligands under inert conditions.
3.2. Experimental

3.2.1. Chemicals: Iron (0) pentacarbonyl (Fe(CO)$_5$, 99.5%), chromium (0) hexacarbonyl (Cr(CO)$_6$, 99%), 1-octadecene (ODE, 90%), oleylamine (OAm, 70%), hexadecylamine (HDA, 98%), hydrochloric acid (HCl, 1.0 M in diethylether), hexanes (95%), and ethanol (EtOH, 200 proof) were purchased from Sigma-Aldrich and used without further purification.

3.2.2. Synthesis

**Fe$_x$Cr$_{1-x}$ Alloy Nanoparticle Synthesis:** In a typical Fe$_x$Cr$_{1-x}$ NP synthesis, 200 mL of ODE, 1.5 g HDA·Cl, and 3 mL of OAm was combined and degassed at 120 °C for 1 h. This mixture was then cooled to RT. Under Ar blanket, 3.76 g of solid Cr(CO)$_6$ and 4.0 mL of Fe(CO)$_5$ were added to the above solution without raising the temperature. The solution was heated to 180 °C in a four-neck flask under slow N$_2$ flow. After annealing for 1 h at 180 °C, the reaction product was cooled to room temperature, and then precipitated with dry ethanol for analysis.

**High temperature Annealing Experiments:** During these experiments NP samples were annealed in a small round bottom flask at a target temperature for specified hours. Annealing took place in open air, allowing O$_2$ exposure. 0.5 mL of stock Fe$_x$Cr$_{1-x}$ alloy NPs were added to 5 mL ODE under inert conditions. To prevent aggregation, 0.1 mL of oleylamine was added as well. The temperature was raised to T = 100, 150 °C and the solution was allowed to anneal for t = 1, 2.5, 5, 12, 24 hours. The solution was then cooled and precipitated in dry ethanol using the previously described cleaning procedure and stored in hexanes for subsequent analysis.

3.2.3. Instrumentation: TEM imaging was performed at the N.C. Brown Center for Ultrastructure Studies at SUNY-ESF, Syracuse, NY using a JEOL JEM 2100F field emission transmission
electron microscope operated at 200 kV, equipped with a 4K CCD camera (Gatan), STEM detector (Gatan) and an EDS detector (Oxford Instruments). Samples were drop cast onto a 300-mesh ultra-thin type A carbon copper grid (Ted Pella). Particle size and aspect ratio were analyzed manually, and statistical analysis was performed using either ImageJ or Corel Draw software on populations of at least 100 counts. Powder X-ray diffraction (XRD) patterns were taken on a Bruker D8-Advance powder diffractometer that utilized Cu-Kα X-rays (λ = 1.5406 Å). The diffraction (Bragg) angles (2θ) were scanned over 20-80° at a step size of 0.04° with a scan speed of 20 sec/step. Samples were dried and loaded on a zero-diffraction SiO₂ crystal (MTI Corp.).

3.3 Results and Discussion

3.3.1. Oxidation at 100 °C

Figure 3.2. TEM image for as-synthesized FeₓCr₁₋ₓ nanocubes over a large area (a) and the HRTEM of a single nanoparticle and the observed lattice spacings (b).
Figure 3.2 shows the in cube-shaped Fe₄Cr₁₋ₓ alloy nanoparticles an average edge size of a = 28.9 ± 2.8 nm. While the large area image indicates highly cubic NPs, a zoomed in picture reveals that these have rounded edges and relatively higher circularity than a purely cubic NP. HRTEM reveals the NP has a metallic center and top edge, evidenced by the metallic <110> planes (d = 2.0 Å). Slanted edge corresponds to unusual <220> metal oxide plane (d = 3.0 Å), instead of the typical <311> plane. M₃O₄ <400> plane at the top is also observed (d = 2.11 Å).
Figure 3.3. TEM image for Fe\textsubscript{x}Cr\textsubscript{1-x} nanocubes oxidized at 100 °C for 1 h (a), 2.5 h (b), 5 h (c), and 12 h (d). Inset in (c) shows an outline representative of NPs oxidized for 5 h.

Figure 3.3 shows the TEM images for Fe\textsubscript{x}Cr\textsubscript{1-x} alloy nanoparticles after oxidation at 100 °C for various times. When NPs are heated in open air for 1 h, as shown in Figure 3.3a, they show almost no change in morphology when compared to as-synthesized NPs. Cubes are very homogenous, with the edge size of $a = 23.5 \pm 2.3$ nm, which is smaller than expected. This smaller size is likely closer to the actual size of as-synthesized NPs, where overlapping NPs made it a bit difficult to correctly identify NP boundaries. When heated for 2.5 h, there doesn’t seem to be much change in the NP morphology, but the average edge size increases to $a = 26.5 \pm 2.8$ nm. With longer oxidation times however, we start observing pinhole voids in the NP corners. Figure 3.3(c, d) show the TEM images of oxidized Fe\textsubscript{x}Cr\textsubscript{1-x} nanocubes annealed at 100 for 5 and 12 h, respectively. Fe\textsubscript{x}Cr\textsubscript{1-x} NPs now have distinctly separated core and shell layers, with point voids between the layers. This point void is a likely a pinhole for core diffusion and appears to be an early snapshot of vacancy coalescence phenomenon observed in our previous work.\textsuperscript{237} This diffusion of core and formation of oxide shell comes with size increase, as evidenced by increased edge sizes of $a = 27.0 \pm 3.2$ nm and $a = 28.7 \pm 2.6$ nm, for (c) & (d), respectively. Increase in the annealing time did not induce any increase in numbers of voids per NP or the void size. In general, for heating periods up to 12 hours, shape deformations from the existing cubic morphology is not observed. When heated for $t = 24$ h (TEM not shown), noticeable NP melting is observed along with the formation of previously observed core/void/shell morphologies.
HRTEM analysis of Fe$_x$Cr$_{1-x}$ nanocubes oxidized at 100 °C revealed evidence of core diffusion, oxide shell formation, and presence of various metal and metal oxide planes. NPs typically maintained metallic character at the center of NP and had oxide formation at the edges and corners. Figure 3.4(a) shows the HRTEM for NPs oxidized for 5 h, and the center (i) shows strongly metallic character with lattice spacing corresponding to b.c.c. <110> plane (d = 2.0, 2.03 Å; at 44.6° on the XRD pattern). On the top edge (ii), oxide formation of has already begun, with lattice plane corresponding to <311> plane of M$_3$O$_4$ (d = 2.45 Å; at 35.5° on the XRD pattern). Figure 3.4(b) shows the HRTEM for NPs oxidized for 12 h, and the extent of oxidation is higher in this case. Center (i) part of the NP now shows presence of oxides with lattice spacing corresponding to oxide <400> plane (d = 2.11, 2.12 Å; at 43.1° on the XRD pattern). On the side edge (ii), stable oxides corresponding to <311> plane of M$_3$O$_4$ (d = 2.52 Å; at 35.5° on the XRD pattern) are formed.
**3.3.2. Oxidation at 150 °C**

![Image of TEM images for Fe<sub>x</sub>Cr<sub>1-x</sub> nanocubes oxidized at 150 °C for 1 h (a) and 5 h (b).](image)

Figure 3.5. TEM image for Fe<sub>x</sub>Cr<sub>1-x</sub> nanocubes oxidized at 150 °C for 1 h (a) and 5 h (b).

Figure 3.5 shows the TEM images for Fe<sub>x</sub>Cr<sub>1-x</sub> alloy nanoparticles after oxidation at 150 °C for t = 1 h (a) and 5 h (b). NPs heated at 150 °C for t = 1 h, as shown in Figure 3.5a, are cubic and have an edge size of a = 25.9 ± 2.3 nm. At closer inspection, formation of internal vacancies is noted, however, this was not observed in the NPs heated at 100 °C, (shown in Figure 3.3a). When heated for 5 h, NPs oxidize completely and form spherical products with average diameter of d = 34.5 ± 4.0 nm, which matches to a similar volume cube with a = 27.8 nm. These spherical NPs have a distribution of either filled spinel NPs or hollowed out oxide spheres.

HRTEM analysis of Fe<sub>x</sub>Cr<sub>1-x</sub> nanocubes oxidized at 150 °C revealed complete oxidation and hollowing of NPs due to faster core diffusion. Figure 3.6 shows the HRTEM for NPs oxidized for 5 h, and the top shows completely oxidized NP with lattice planes corresponding to <311> plane of M₃O₄ (d = 2.48 Å; at 35.5° on the XRD pattern). NPs at the bottom also reveal similar oxide lattice planes, but also show partial or complete hollowing of the alloy core.
Figure 3.6. HRTEM image for Fe$_x$Cr$_{1-x}$ nanocubes oxidized at 150 °C for 5 h.

Table 3.1. Size and shape data for the as-synthesized and oxidized Fe$_x$Cr$_{1-x}$ NPs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shape</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Synth NPs</td>
<td>cubes with rounded edges</td>
<td>a = 28.9 ± 2.8</td>
</tr>
<tr>
<td>100 °C + 1 h</td>
<td>cubes</td>
<td>a = 23.5 ± 2.3</td>
</tr>
<tr>
<td>100 °C + 2.5 h</td>
<td>cubes</td>
<td>a = 26.5 ± 2.8</td>
</tr>
<tr>
<td>100 °C + 5 h</td>
<td>cubes with voids</td>
<td>a = 27.0 ± 3.2</td>
</tr>
<tr>
<td>100 °C + 12 h</td>
<td>cubes with voids</td>
<td>a = 28.5 ± 2.6</td>
</tr>
<tr>
<td>100 °C + 24 h</td>
<td>cubes with voids + core/void/shell</td>
<td>d = 17.2</td>
</tr>
<tr>
<td>150 °C + 1 h</td>
<td>cubes with voids</td>
<td>a = 25.9 ± 2.3</td>
</tr>
<tr>
<td>150 °C + 5 h</td>
<td>cubes with voids + hollow spheres</td>
<td>d = 34.5 ± 4.0 (a = 27.8 nm)</td>
</tr>
</tbody>
</table>
3.3.3. Extent of Oxidation and Void Formation as a Function of Temperature

Table 3.2. Data from the HRTEM images: identified lattice planes and the ratio of oxide shell to the NP size for the as-synthesized and oxidized Fe\textsubscript{x}Cr\textsubscript{1-x} NPs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>identified Lattice Planes</th>
<th>NP size (a, in nm)</th>
<th>Shell thickness (ts, in nm)</th>
<th>ts/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Synth NPs</td>
<td>Metallic &lt;110&gt;, M\textsubscript{3}O\textsubscript{4} &lt;220&gt; &amp; &lt;400&gt;</td>
<td>a = 28.9 ± 2.8</td>
<td>1.5</td>
<td>0.052</td>
</tr>
<tr>
<td>100 °C + 5 h</td>
<td>Metallic &lt;110&gt;, M\textsubscript{3}O\textsubscript{4} &lt;311&gt;</td>
<td>a = 27.0 ± 3.2</td>
<td>2.5</td>
<td>0.092</td>
</tr>
<tr>
<td>100 °C + 12 h</td>
<td>M\textsubscript{3}O\textsubscript{4} &lt;220&gt;, &lt;400&gt;, &amp; &lt;311&gt;</td>
<td>a = 28.5 ± 2.6</td>
<td>4.8</td>
<td>0.168</td>
</tr>
<tr>
<td>150 °C + 5 h</td>
<td>M\textsubscript{3}O\textsubscript{4} &lt;311&gt;</td>
<td>d = 34.5 ± 4.0</td>
<td>7.9</td>
<td>0.263</td>
</tr>
</tbody>
</table>

Figure 3.7. The ratio (ts/a) of oxide shell thickness to edge size is compared for Fe\textsubscript{x}Cr\textsubscript{1-x} NP samples annealed in various oxidation environments.
Crystallinity and the oxidation in Fe<sub>x</sub>Cr<sub>1-x</sub> NPs was analyzed via powder X-ray diffraction analysis. Figure 3.8 shows the two oxidation environments where NPs were oxidized at 100 °C (a) & 150 °C (b). XRD patterns for NPs oxidized at 100 °C show strongly metallic, crystalline nature and intense b.c.c. <110> reflection at 44.6° for all the samples. Oxide reflection is minor and starts to appear as a minor bump at 35.5° as the oxidation temperature goes up. When heated at 150 °C, metallic pattern is observed at t = 1 h, along with minor oxide reflection. Complete oxidation is observed only at t= 5 h, which is also corroborated by the HRTEM analysis in Figure 3.6.
3.4. Conclusions
Cube shaped Fe$_x$Cr$_{1-x}$ NPs were synthesized by co-decomposition of metal carbonyl precursors in presence of organic ligands. NPs were oxidized at various annealing conditions to understand the high temperature diffusion in binary stainless-steel alloy nanoparticles. Oxidation and diffusion were studied using TEM and XRD. TEM images were obtained at various annealing condition and NPs showed cubic morphology. Pinhole voids form after annealing at 100 °C (t = 5 h), & continues for t=12h, but NPs degrade at t=24 h. There is no indication of increase in void size or the total number of voids. High Temperature annealing at 150 °C for 1h also forms similar cubes with pinholes but increasing this annealing time (t = 5 h) results in a mixture of cubes & spheres NPs. Minor number of core/void/shell NPs are also formed in this synthesis. HRTEM analysis suggests presence of various metal and M$_3$O$_4$ layers form at the surface of the alloy NP. At the center of NP metallic b.c.c. planes (<110>) are seen while <400>, <220> & <311> M$_3$O$_4$ planes are prominent at the edges. Oxide shell grows as the annealing time go up. XRD data shows that Fe$_x$Cr$_{1-x}$ alloy NPs are highly crystalline. While surface oxide layers are noticeable in the HRTEM in Figure 3.4, XRD patterns for the same samples do not show strong oxide reflections after open air heating at 100 °C, however, <311> peak shows gradual increase. Complete oxidation is seen only after heating in open air at 150 °C for 5 h.
Chapter 4

Alloying and Phase Transformation in Fe/Fe<sub>x</sub>Ni<sub>1-x</sub> Core/Alloy Nanoparticles

In this work I describe the how interfacial thermodynamics dictates the alloying and phase behavior of Fe/Fe<sub>x</sub>Ni<sub>1-x</sub> Core/Alloy nanoparticles (CA-NPs) as a function of annealing temperature. The importance of interfacial effects on thermodynamics and diffusion kinetics is described and examined in light of the observed temperature dependent alloying of synthesized Fe/Ni core/shell nanoparticles into Fe/Fe<sub>x</sub>Ni<sub>1-x</sub> core alloy nanoparticles, which is observed to occur in a highly controllable manner, with final alloy compositions that resemble Fe/Ni intermetallics with increased γ-phase composition, and Invar steels. The improved grain boundary diffusion rates between Fe and Ni, favorable mixing enthalpy (ΔH<sub>mix</sub>), low phase segregation enthalpy (ΔH<sub>Seg</sub>), and highly crystalline nature of the nanoparticle itself were found to be the primary drivers of this unique processability. Finally, the results indicate that at temperatures above 300 °C the nanoparticles begin to contain internal carbons in the form of metal carbides, which suggest that the typically inert monolayer encapsulation can also lead to new phases and properties. The outlook of this technique for ternary and quaternary compositions is evaluated and its importance to the design of new materials.

4.1. Introduction

The ability to synthesize nanoparticles resembling steels from a purely synthetic inorganic nanochemistry approach would allow for the development of nanometer-thin metal, magnetic and stainless coatings, as well as robust lubricants, and new additive manufacturing ingredients. Such steel nanoparticles could then be used to endow composites, plastics, and textiles with magnetic,
electrical, and structural properties inherent to bulk steels at a fraction of the overall mass. For example, the Fe-Ni base alloys display stainless behavior while retaining high magnetization and strength, leading to broad applications in turbines, heat exchangers, and manufacturing infrastructure.\textsuperscript{358} Specialty alloys of Fe-Ni include Invar steels (Fe\textsubscript{0.64}Ni\textsubscript{0.36}) which play a vital role in electronics and precision instruments due to its negligible thermal expansion,\textsuperscript{359} as well as higher content Ni steels for electromagnetic shielding.\textsuperscript{358}

The transition to the nanoscale holds great promise for endowing materials with these same properties through thin films, as well as providing new opportunities for biomedical imaging agents\textsuperscript{360} and high efficiency catalysts.\textsuperscript{26} The development of Fe/Ni NPs are of particular interest due to their high magnetization\textsuperscript{361} and tunable compositions\textsuperscript{362} including that of Invar,\textsuperscript{363,364} with demonstrated potential as microwave absorbers,\textsuperscript{365,366} hydrazine catalysts,\textsuperscript{367,368} and electrochemical glucose sensors,\textsuperscript{369} To realize this potential, however, an understanding of the thermodynamic and kinetic factors which drive alloying is necessary. Specifically, the promise of enhanced diffusion at the nanoscale\textsuperscript{338} and improved mixing enthalpies\textsuperscript{370–372} for low temperature alloy NP synthesis must be contrasted with a higher importance of surface energies and interfacial strain,\textsuperscript{373} which continues to be a subject of intense theoretical research for describing equilibrium alloy structures.\textsuperscript{374,375} The refinement of these models, however, hinges upon the accumulation of experimental data related to the changes of multi-metallic NPs as a function of time and temperature.\textsuperscript{375,376}

We have been developing a core-alloy (CA) approach towards crafting alloy nanoparticle interfaces. By focusing on crafting and depositing an alloy only at a pre-formed nanoparticle interface, I have attempted to overcome challenges often faced by synthetic inorganic chemists and materials scientists preparing alloy nanoparticles by mixing metal salts followed by co-
reduction, electrochemical reduction, performing galvanic displacement, or thermal treatment, where differences in redox potentials, decompositions, and precursor reactivity makes controlling the final alloy composition, distribution, and phase homogeneity difficult. The CA approach focuses on depositing, alloying, or exchanging nanometer thin layers of solute atoms at the interface of a pre-formed metallic nanoparticle. A key to this approach is the slow sequential deposition of sub-monolayer to monolayer thicknesses of a solute metal, originating from an organometallic precursor (i.e., metal carbonyls), at a crystalline pre-formed nanoparticle. This allows for metallic alloying to occur, instead of rapid galvanic exchange between the solute precursor and the nanoparticle. Previous core alloy studies have focused on substantiating the approach, and implementing different metal combinations, namely; AuAg, AuPd, AuAgPd, FeCr, FeNiCr and FeCrNi at modest annealing temperatures of 100-180 °C.

In this work understanding of the core-alloy approach using a Fe/Fe$_{x}$Ni$_{1-x}$ nanoparticle is expanded by studying the alloying and phase change during elevated temperature annealing using X-ray diffraction (XRD). In addition to temperature dependent alloying, the experimental results also show that carbides are formed at higher temperatures.

4.2. Experimental

4.2.1. Chemicals: Iron (0) pentacarbonyl (Fe(CO)$_{5}$, 99.5%), (bistriphenyphosphine)dicarbonyl nickel (0) (Ni(PPh$_{3}$)$_{2}$(CO)$_{2}$, 98% anhydrous), oleylamine (OAm, 70%), 1-octadecene (ODE, 90%), dioctylether (DOE, 99%), tetrahydrofuran (THF, anhydrous, ≥99.9%), hexadecylamine (HDA, 98%), hydrochloric acid (HCl, 1.0 M in diethylether), hexanes (95%), and ethanol (EtOH, 200 proof) were purchased from Sigma-Aldrich and used without further purification.
4.2.2. Synthesis

**α-Fe Nanoparticle Synthesis:** Crystalline α-Fe nanoparticles were prepared according to a previous method. In a typical α-Fe synthesis, 15.0 mL of ODE, 100.0 mg HDA·Cl, and 0.5 mL of OAm was combined and degassed at 120 °C for 0.5 h. This mixture was then heated to 180 °C in a four-neck flask under Ar, and 0.2 mL of Fe(CO)₅ was injected under Ar. The solution was agitated through shaking and Ar bubbling to avoid collection of the NPs on a magnetic stir-bar. After annealing for 0.5 h at 180 °C, ~5 mL of the reaction volume was removed, cooled to room temperature, and then precipitated with dry ethanol for analysis. The un-cleaned α-Fe aliquots were kept in the reaction vessel under Ar gas and used as the core for nickel deposition, as described next.

**Nickel Deposition at α-Fe Cores (α-Fe/FeₓNi₁₋ₓ):** Next, nickel was deposited at the α-Fe NP cores, keeping the temperature same. During shell deposition, 5 mL solution of Ni(PPh₃)₂(CO)₂ (0.5 M in THF) was injected into the remaining solution of α-Fe cores synthesized above. Amount of shell precursor is calculated for a target Ni shell thickness of 1 nm. Total volume of Ni(PPh₃)₂(CO)₂/THF solution was split into ten separate injections (0.5 mL each) to maintain steady annealing temperature, with 15 minutes of annealing time between injections. After completing Ni precursor injections, the reaction was let to cool to room temperature. The NPs were purified by precipitation in dry ethanol (200 proof) under Ar. After centrifugation (10 min, 4400 RPM), the product was re-dispersed in dry hexane and stored under Ar.

**High temperature Annealing Experiments:** During these experiments NP samples were annealed in a small round bottom flask at a given temperature for 5 hours. Annealing took place under Ar flow and precautions were taken to limit O₂ exposure. 0.5 mL of stock Fe/Ni core/shell NPs (≈720 mg) were added to 5 mL ODE under inert conditions. To prevent aggregation, 0.1 mL
of oleylamine was added as well. The temperature was raised to the target ($T = 250 \, ^\circ\text{C}, 310 \, ^\circ\text{C},$ and $325 \, ^\circ\text{C}$) and the solution was allowed to anneal for 5 hours. The solution was then cooled and precipitated in dry ethanol using the previously described cleaning procedure, and subsequent analysis was conducted.

4.2.3. Instrumentation: TEM imaging was performed at the Upstate Medical University, Syracuse, NY using a JEOL 2000 transmission electron microscope operated at 200 kV, equipped with a LaB$_6$ filament and 4K CCD camera. Samples were drop cast onto a 300-mesh ultra-thin type A carbon copper grid (Ted Pella). Powder X-ray diffraction (XRD) patterns were taken on a Bruker D8 Advance powder diffractometer that utilized Cu-Kα X-rays ($\lambda = 1.5406 \, \text{Å}$). Samples were dried and loaded on a zero-diffraction SiO$_2$ crystal (MTI Corp.). The reference data were obtained from the PDF-4+ database (ICCD) for identification and comparison. The corresponding lattice constants were calculated using Bragg’s law given by:

$$2d \sin \theta = n\lambda$$

where $\theta$ is the diffraction angle, $n$ is an integer taken as unity, $\lambda$ is the X-ray wavelength, and $d$ is related to the Miller indices of the FCC lattice by $d = a \left(h^2 + k^2 + l^2\right)^{-1/2}$. Similarly, the grain size ($\tau$) was estimated using the Scherrer equation given by:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where $K$ is a dimensionless factor taken near unity (0.9 for near spherical objects), $\beta$ is the peak broadening (full width half maximum) in radians, and $\theta$ is the diffraction angle in radians. The Fityk software package was used to confirm the lattice constants obtained from the $<111>$ indice peak reflections in Figure 4.2 and for the analysis of the lower intensity $<200>$ and $<220>$
reflections revealing that the actual composition is likely 8-10% lower than that calculated from the <111> reflection.

4.3. Results and Discussion

To study the alloying of Fe/FeₓNi₁₋ₓ NPs, I started by first synthesizing crystalline α-Fe NPs,²⁵¹,³⁰⁵ capped with a mixture of oleylamine (OAm) and hexadecylammonium chloride (HDA·Cl) ligands. This was followed by the deposition of metallic Ni onto the α-Fe by the thermal decomposition of Ni(CO)₂(PPh₃)₂ at T = 180 °C, resulting in a f.c.c. rich Ni shell interface.

![Figure 4.1](image.png)

**Figure 4.1.** Representative TEM micrographs for α-Fe core (a), as-synthesized Fe/Ni NPs at 180 °C (b), after annealing at 250 °C (c), 310 °C (d), and 325 °C (e). Scale bar corresponds to 50 nm.

Deposition of Ni shell leads to small increase in diameter (d) increase from \(d_{Fe} \approx 17.7 \pm 3.1\) to \(d_{Fe/Ni} \approx 19.6 \pm 2.6\) nm, as show in Figure 4.1 (a, b). The synthesized Fe/FeₓNi₁₋ₓ NPs were
then thermally annealed at temperature $T \geq 250 \, ^\circ C$ for 5 h. Figure 4.1(c-e) show that this annealing results in aggregation and melting of Fe/Fe$_x$Ni$_{1-x}$ NPs.

4.3.1. Evidence for Phase Transition via X-ray Diffraction Analysis

![Graph](image)

**Figure 4.2.** Representative XRD of Fe/Ni NPs synthesized at 180 °C (i), and after annealing for 5h at 250 °C (ii), 325 °C (iii) (a). Plot of the lattice constant ($a$, closed circles) obtained from the XRD peak shifts of the <111> planes after analysis with Fityk software, and grain size ($\tau$, open circles), as a function of annealing temperature (T) (b). Plot of $a$ vs. Fe content (%) with experimental data overlaid.

Crystal structure, phase transition, and alloying in Fe/Fe$_x$Ni$_{1-x}$ CA-NPs were investigated via powder X-ray diffraction (XRD). Shifts in metallic reflections, and introduction of new peaks in the XRD data was used to confirm phase change and/or the level of alloying. Figure 4.2(a) shows a set of representative powder XRD results for the Fe/Ni as-synthesized (i) and after
annealing at 250 °C (ii) and 325 °C (iii). In general, XRD showed <110> and <111>, <200> reflections confirming presence of highly crystalline α-Fe (b.c.c.), & Ni (f.c.c.), respectively. At the same time however, no <311> metal oxide (M₃O₄, M= Fe, Ni) reflections are visible, which is not surprising due to the air-free conditions maintained during the synthesis and further annealing steps.

The as-synthesized Fe/Ni shows two key characteristics. First, there is an overlay of b.c.c. α-Fe (2θ<110> = 44.6°) and f.c.c. Ni (2θ<111> = 44.4°) signatures, but also <200> at 2θ = 51.9 and <220> at 75.6° (not shown), respectively, which are indicative of a crystalline Ni shell. Upon annealing at 250 °C (ii), there are pronounced shifts in the <111>, <200>, and <220> reflections to lower 2θ, indicating an increasing Fe content in the growing Fe/Ni alloy phase. Shifting of diffraction peaks to a lower 2θ may indicate an increase in the lattice parameter or improved f.c.c. character. Here, the Fe atoms at the center of the NP alloy and diffuse into the Ni atoms at the interface, the NP adopts a more f.c.c. character. In the top insert of Figure 4.2a-i shows the f.c.c. γ-Fe crystal structure, as alloying occurs, the lattice constant (a) expands accordingly. The reference indices shown in (ii) correspond with FeNi₃ and Fe₃Ni₂, and as shown the NP has transformed to a composition in-between these phases. For example, intermediate structures such as FeNi₃ forms a primitive cubic (P221) structure, which matches up well. At 325 °C (iii), the <111> now resides close to the Fe₃Ni₂ phase, indicating continued alloying at that temperature. Metallic peak also matched up with austenite steel (SS304) which is γ-stainless steel, with varied compositions such as Fe₃Ni₂, FeCrNi/C, and FeNi/C. Interestingly, new broad reflections are observed which do not index well with oxides. However, many of these new peaks correspond with carbide rich compositions, such as γ-Fe₅C₂ suggesting that the Fe-composition at the interface
has further increases, and as well, that the ligands in solution are decomposing, providing the carbon-source.

To gain more insight into the temperature induced phase changes, the primary reflection $<111>$ was analyzed lattice constant ($a$) and the grain size ($\tau$). Figure 4.2(b) plots $a$ (bottom, closed circles) and $\tau$ (top, open circles) of the $<111>$ with alloying $T$. While the $a$-increases with $T$, (Figure 4.2(b) bottom), $\tau$ remains relatively constant (Figure 4.2(b), top) during the annealing process. Figure 4.2(c) uses XRD standards for Fe/Ni alloys, and a Vegard’s relationship between composition and the observed lattice parameter was used to determine concentrations. For instance, by first synthesizing a Fe/Ni NP with a controlled core-to-shell volume ratio, in this case $\sim 2.5$, and by annealing at $325 \, ^\circ C$, one can expect a NP interface rich in a $\approx Fe_{0.43}Ni_{0.57}$ composition.

Previous studies of Fe-Ni alloy NPs have found that phase precipitation occurs when the content of Fe is increased beyond $70\%$,\textsuperscript{385–387} which is similar to observations in bulk Fe-Ni alloys,\textsuperscript{388} but no phase precipitation (indicated by strong reflections at $44.6^\circ$ and $65^\circ$) is observed in this system. Calculation of $a$ using the $<200>$ and $<220>$ reflections shows a lower Fe content with increasing annealing temperature, suggesting the true alloying content is below the phase segregation threshold. Interestingly, Monte Carlo simulations involving Fe rich Fe/Ni alloys have predicted an external bcc-Fe shell and $\gamma$-FeNi core,\textsuperscript{389} this configuration was not observed here.
Figure 4.3. X-ray photoelectron spectra for 2p binding energy regions of Fe and Ni for Fe/Fe$_x$Ni$_{1-x}$ CA-NPs annealed at 180 °C (i), 250 °C (ii), 310 °C (iii), and 325 °C (iv).

In order to quantify the exact composition and oxidation states of Fe/Fe$_x$Ni$_{1-x}$ CA-NPs were analyzed via X-ray photoelectron spectroscopy. Compositional analysis showed that metallic and oxygen composition gradually decreased as a function of annealing temperatures. On the other hand, increased higher carbon content points towards formation of carbon rich alloys such as FeNi$_3$C, austenite steel. Table 4.1 shows that while Ni showed higher surface composition at lower temperatures, Fe diffusion from the core led to increase in Fe composition at higher temperatures.

Metallic oxidation states were analyzed in 2p binding energy (B.E.) regions of Fe & Ni, showed interesting results due to interplay of surface diffusion and temperature. For as-synthesized Fe/Fe$_x$Ni$_{1-x}$ NPs, Fe 2p$_{3/2}$ binding energy region showed a broad peak that was deconvoluted to obtain two peaks corresponding to Fe$_3$O$_4$ at 709.5 eV, and Fe$_2$O$_3$ at 712.75 eV (Figure 4.3-i, ii). Analysis of the Ni 2p$_{3/2}$ region shows presence of broad peak corresponding to NiO/Ni$_2$O$_3$ with a
shift to higher B.E at 855.5 eV. For Fe/Fe$_x$Ni$_{1-x}$ NPs annealed at 250 °C, Fe 2p peaks are even broader with almost similar peak structure. Ni 2p$_{3/2}$ region shows an additional Ni$^0$ peak at 850.0 eV, along with previously observed NiO/Ni$_2$O$_3$ peaks. In case of CA-NPs annealed at higher temperatures (310 °C & 325 °C), broader B.E. peaks are observed in both Fe 2p and Ni 2p regions. In the Fe 2p$_{3/2}$ region, peaks for Fe$^0$ at 705.75 eV, 706.25 eV, oxide or carbide species at higher eV are seen, and in the Ni 2p$_{3/2}$ region peak for Ni$^0$ is seen at 852.75 eV. Lack of Ni at the surface results in low intensity peaks for the NPs annealed at high temperatures, as shown in Figure 4.3-iii, -iv. Presence of zero oxidation state metal peaks is indicative of core diffusion and redistribution of surface oxygen. Larger numbers of peak deconvolutions also suggest increased number of surface species.

Overall, at lower annealing temperatures of 180 °C & 250 °C, minor peak shift to higher B.E. is observed, denoting formation of newer species, but lower number of deconvolutions confirms smaller number of detected species. Increase in temperature led to lower metal composition with formation of several new species, as well as the zerovalent standard metallic peak.

Table 4.1. XPS determined % composition of Fe & Ni in for Fe/Fe$_x$Ni$_{1-x}$ CA-NPs.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fe (%)</th>
<th>Ni (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Fe$<em>x$Ni$</em>{1-x}$ (180 °C)</td>
<td>45.80</td>
<td>54.20</td>
</tr>
<tr>
<td>Fe/Fe$<em>x$Ni$</em>{1-x}$ (250 °C)</td>
<td>33.33</td>
<td>66.67</td>
</tr>
<tr>
<td>Fe/Fe$<em>x$Ni$</em>{1-x}$ (310 °C)</td>
<td>78.16</td>
<td>21.84</td>
</tr>
<tr>
<td>Fe/Fe$<em>x$Ni$</em>{1-x}$ (325 °C)</td>
<td>78.858</td>
<td>21.15</td>
</tr>
</tbody>
</table>

Table 4.2. XPS binding energy (B.E.) values for Fe/Fe$_x$Ni$_{1-x}$ CA-NPs.
### Reaction Table

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fe 2p (eV)</th>
<th>Ni 2p (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1/2)</td>
<td>(3/2)</td>
</tr>
<tr>
<td>Fe/Fe₅Ni₁₋ₓ (180°C)</td>
<td>724.50</td>
<td>709.5, 712.75</td>
</tr>
<tr>
<td>Fe/Fe₅Ni₁₋ₓ (250°C)</td>
<td>726.50</td>
<td>710, 713.5</td>
</tr>
<tr>
<td>Fe/Fe₅Ni₁₋ₓ (310°C)</td>
<td>725.5, 730</td>
<td>705.75, 708.25, 709.5, 713.25</td>
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<tr>
<td>Fe/Fe₅Ni₁₋ₓ (325°C)</td>
<td>721, 725.5</td>
<td>706.25, 708.5, 710.5, 712.25</td>
</tr>
</tbody>
</table>

### 4.3.2. Alloying and Segregation at the Nanoscale

In order to understand the role of theoretical mixing and segregation enthalpies on alloying and phase transition in the Fe/Ni core/shell NPs, I collaborated with Dr. Tennyson Doane, then postdoctoral associate in the Maye research group. We observed that, Iron and nickel alloy into a variety of different compositions and phases, as described empirically by the Fe-Ni bulk phase diagram. In general, Fe-Ni binary alloys are miscible at higher temperatures, with many mixed phases and intermetallics possible at lower temperatures. While the phase diagram predicts the behavior of mesoscale thin films and bulk metals, at the nanoscale and particularly in the sub 50 nm size regime alloying is highly dependent upon composition, size, and shape, as well as synthesis conditions and routes (i.e., precursors, ligands, etc.). Generally speaking, a NP synthesized in a synthetic inorganic manner is far away from the global thermodynamic minima, since nucleation and growth timeframes are micro- to millisecond, concentrations are dilute, and temperatures are typically <100 °C. Thus, simple synthesis alone may not provide favorable conditions to craft uniform NP alloys like those found in steel, and thus a thermal annealing step is required.
Alloying is driven by favorable mixing enthalpy ($\Delta H^{\text{Mix}}$), and also by the tendency to minimize interfacial energies at the nanoscale, both between the core and the shell as well as between the NP and the local environment. The core-shell interfacial energy arises due to the strain developed as the shell adjusts to match the underlying core lattice structure, which can lead to defects and stacking faults. Figure 4.4(b) shows the corresponding plot of $\Delta H^{\text{Seg}}$ for the binary Fe/X and X/Fe solvent-solute mixtures, showing that for 3d metals the values are quite similar suggesting only a weak segregation driving force (centered around the origin); in contrast, Al, Mo, and W all have significant segregation preferences that might inhibit alloying. In the case of Fe-Ni, Figure 4.4(b) shows only a weak preference of Ni on the NP surface suggesting that segregation will not be a significant barrier to alloying. Furthermore, as Ni only grows epitaxially on Fe for a few monolayers before forming a f.c.c. lattice with a high degree of lattice mismatch ($a_{\text{b.c.c. Fe}} = 2.87$ Å and $a_{\text{f.c.c. Ni}} = 3.52$ Å), the strain produced in a core-shell architecture is expected to be a much stronger positive influence for alloying at the nanoscale.

Figure 4.4. Plots of the mixing enthalpies, $\Delta H^{\text{Mix}}$ (a) and $\Delta H^{\text{Seg}}$ (b) of different binary Fe-X couples relevant to steel for predicting alloying in the bulk. The arrows indicate the general trends expected for alloying and segregation at the nanoscale. (Theoretical analysis and figure courtesy of Dr. Tennyson Doane)
Taken together, the results show that (1) the alloying of Fe and Ni was preferred thermodynamically as suggested by the macroscopic atom model, as indicated by the systematic evolution of lattice constant, as shown by XRD; (2) the phase boundaries for the $\gamma$-FeNi transformation was lowered relative to the bulk, as indicated by alloying occurring at modest temperatures in this system (180–325°C); and that (3) interfacial diffusion between two concentric layers in a NP can be used to promote alloying in the periphery. In addition, the observation that little oxide is formed suggest a degree of stainless behavior in these NPs, and that at the higher temperatures (325 °C), that XRD reflections consistent with carbides were also observed, suggesting a further way to tailor composition, phases and properties in future versions of nanoparticle steels.

4.4. Conclusion:

In conclusion the experimental alloying and Phase behavior of Fe/Fe$_x$Ni$_{1-x}$ core/alloy NPs was investigated using X-ray diffraction and examined in light of empirical bulk thermodynamic and diffusion data to establish a general framework for predicting alloying behavior in multi-component transition metal alloys in the future. Fe/Fe$_x$Ni$_{1-x}$ CA-NPs were synthesized using air-free Schlenk line techniques by high temperature co-decomposition of precursors in presence of surface capping ligands, and further annealed at higher temperatures under inert conditions. Annealing of Fe/Fe$_x$Ni$_{1-x}$ NPs led to shift in diffraction peaks to a lower 2\(\theta\) value, showing phase change to $\gamma$-rich composition. In addition to modulating the shell composition as a function of temperature, it was also found that at higher temperatures (>300 °C) additional features due to carbide formation were observed, presumably due to organic ligand decomposition. While acknowledging that additional strain, stress, and depletion will play a major role in chemical
ordering at the nanoscale, the current framework provides a practical foundation for predicting whether or not the alloying between core and shell will occur, and the effects that annealing temperature will have on NP transformations.
Chapter 5

Summary and Outlook

The key focus of my work is the study of oxidation and morphology evolution in transition metal nanoparticles of varying compositions. In this thesis, I discuss the oxidation in Fe/FeCrNi core/shell NPs, Fe_{x}Cr_{1-x} core/alloy NPs, morphological evolution in Fe_{x}Cr_{1-x} alloy NPs, and the phase transition in the Fe/Fe_{x}Ni_{1-x} NPs. In the thesis, I also describe the wet chemistry approach to synthesizing multi-shell Fe/Cr_{x}Ni_{1-x} core/alloy NPs, bimetallic Fe_{x}Cr_{1-x} alloy NPs & Fe_{x}Cr_{1-x} core/alloy NPs. I demonstrate the potential of constructing transition metal nanoparticles that retain metallic characters, form internal voids, and undergo phase transition, which may pave the way for performance gains in nano magnetism and conductivity, which in turn could lead to new forms of stainless thin-films, magnetic coatings, and long lasting nano properties.

In chapter 2, I demonstrated the optimized synthesis of mixed shell Fe/FeCrNi core/alloy nanoparticles (CA-NPs), termed as the stainless-steel NPs, due to their superior oxidation resistant properties. Synthesis of mixed shell Fe/Cr/Ni, Fe/Ni/Cr, and Fe/Cr_{x}Ni_{1-x} core/alloy nanoparticles (CA-NPs) is investigated, where chromium and nickel carbonyl-based precursors are used for depositing various shell combinations. Alloying and diffusion at the interface is significantly affected by the shell thickness and shell deposition sequence, and thus we noticed varying levels of oxidation in these samples. Diffusion in Fe/Fe_{x}Cr_{1-x}, Fe/Fe_{x}Ni_{1-x}, and Fe/Cr_{x}Ni_{1-x} core/alloy NP systems is studied using the Cabrera-Mott Theory of oxidation, and Fick’s law of diffusion and the rationale behind the varying levels of oxidation is proposed. Incidentally, CA-NPs showed complete transformation from the α- to a rare, brittle, σ-phase when synthesized at elevated
temperatures. Corrosion studies of these NPs showed their strong stainless properties, making them a strong candidate for an application requiring robust oxidation prevention at the nanoscale.

In chapter 3, I describe the effect of oxidation on the morphological evolution in binary Fe$_x$Cr$_{1-x}$ stainless alloy NPs. Cube shaped Fe$_x$Cr$_{1-x}$ NPs were synthesized by co-decomposition of metal carbonyl precursors in presence of organic ligands. HRTEM analysis of the oxidized alloy NPs reveal the extent of pinhole voids and confirm that the internal void formation in the Fe$_x$Cr$_{1-x}$ nanocubes is highly dependent on oxidation environment.

In chapter 4, experimental alloying and Phase behavior of Fe/Fe$_x$Ni$_{1-x}$ core/alloy NPs was investigated using X-ray diffraction and examined in light of empirical bulk thermodynamic and diffusion data to establish a general framework for predicting alloying behavior in multi-component transition metal alloys. Fe/Fe$_x$Ni$_{1-x}$ CA-NPs were synthesized using air-free Schlenk line techniques by high temperature co-decomposition of precursors in presence of surface capping ligands, and further annealed at higher temperatures under inert conditions. Annealing of Fe/Fe$_x$Ni$_{1-x}$ NPs led to shift in diffraction peaks to a lower $2\theta$ value, showing phase change to $\gamma$-rich composition.

While we have addressed the challenges towards the synthesis of binary transition metal core/shell NPs & alloys with a specific interest in Fe, Cr, and Ni metals, there’s great opportunity for research in creation of other metallic combinations. Carbonyl complexes for transition metals are available commercially, making it easier to copy the synthetic protocol for. In fact, we were able to utilize other metal carbonyls in some of our preliminary synthesis work involving other transition metals. Combining the described theoretical framework and the synthesis protocol would be of remarkable assistance for investigators looking to expand into this research field.
References:


(353) Slaton, R. D. Designing Core/Alloy Nanoparticles by Manipulation of Interfacial Oxidation and Atomic Diffusion, Syracuse University: Syracuse, NY, 2015.


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EDUCATION

Syracuse University 2013-2018
Ph.D. Candidate in Materials Chemistry with Prof. Mathew M. Maye
Thesis: Design and Synthesis of Stainless-Steel Nanoparticles: Oxidation Behavior and Morphological Evolution

Institute of Chemical Technology, Mumbai (formerly UDCT/UICT) 2009-2013
B.Tech. in Organic Colorant Technology; Minors in Chemical Engineering
Thesis Advisor: Prof. Prakash M. Bhathe
Thesis : Employing Design of Experiment to Improve the Synthetic Yield of 1-chloro-4-nitro-anthraquinone

WORK & RESEARCH EXPERIENCE

Materials Chemistry Intern at Pelitex Inc. 2017
• Executed a synthesis scale-up & technology transfer project for a Fortune 500 chemical company in record time.
• Designed safety protocols for materials synthesis at increased scales, and improved waste recycling.
• Collaborated with researchers to optimize the silica shell coating to improve hydrophilicity of products.

X-ray Facility Administrator at Syracuse University 2014-present
• Trained new users on the diffractometer and the necessary safety protocols; coordinated user queue.
• Collaborated with internal & external users for specialized sample prep & data analysis.
• Maintained auxiliary chiller operations, repaired minor breakdowns, scheduled maintenance & inspections.
• As part of my teaching assistant duties, I taught “Solid State Modeling and X-ray Diffraction” lab for chemistry honors students every fall.

Graduate Researcher at Syracuse University 2013-present
• Investigated synthetic design of transition metal core/shell type nanoparticles (NPs) that exhibited hollow internal microstructures. This study of diffusion & oxidation behavior in transition metal NPs is funded by NSF.
• Successfully exploited our findings to improve corrosion resistance in alloys NPs and create truly “stainless” NPs.
• Published several peer reviewed journal articles, co-authored patents, and presented research in regional and national conferences.
• Explored other research topics including - asymmetric internal voids in novel NP systems, sulfidation of Fe/Cr core/shell NPs, reaction monitoring using CsPbX₃ perovskites, ligand exchange, phase transfer, silica coating, & surface functionalization in magnetic NPs, & discrete dipole approximation routines to model electromagnetic absorption and scattering around various noble and transition metal NP geometries.

Teaching Assistant at Syracuse University 2013-present
• Supervised undergraduate trainees & summer REU researchers in the Maye lab.
• Developed 4 new lab modules to introduce advanced materials chemistry topics such as synthesis & properties of NPs. Topics include “Synthesis of Cesium Lead Perovskite (CsPbX₃) nanocrystals”, “Comparing Optical Property of Fluorescent Compounds using Spectrometers”, “Demonstration of Transmission Electron Microscope”, & “Solid State Modeling & X-ray Diffraction
• Received Graduate Teaching Assistant Mentor Award from the Syracuse University Graduate School in 2016 for outstanding mentorship service to the incoming STEM teaching assistants.
Internships

- Summer research intern at ICT Mumbai in a project funded by Dow Industries, performed systematic studies to synthesize an organic dyestuff intermediates. 2011

Technical Skills

- **Synthesis:** Nanoparticles (Transition and Noble Metals, Perovskites, Quantum Dots) · Air-free Techniques (Schlenk Line and Glovebox) · Microwave · Organic Lab work
- **Structural Characterization:** Powder and Single Crystal X-ray Diffraction (Facility Manager for 4+ years)
- **Electron Microscopy:** TEM equipped with EDS & STEM detectors (full user on 3 different JEOL TEMs; trained new users) · SEM (JEOL IT100LA) · EDS Certification from Oxford Instruments · AFM (Bruker Innova)
- **Spectroscopy:** X-Ray Photoelectron Spectroscopy (XPS/ESCA) · NMR · FTIR · UV-Vis · Fluorometer
- **Technical Misc.:** Thermo-gravimetric Analysis (TGA) · Differential Scanning Calorimetry (DSC) · Magnetization in materials · Ultracentrifuge · Spin coater · Sputter coater · Dynamic Light Scattering (DLS) & ζ-potential
- **Computational Analysis:** Discrete Dipole Approximation (DDA) · Familiar with FDTD
- **Softwares:** Origin · Plotly · ImageJ · ChemDraw · Vesta · TEMCON (JEOL) · Digital Micrograph (Gatan) · AZtec (Oxford Instruments) · Bruker Diffrac.Suite · CasaXPS · Illustrator · Corel-Draw · Maya (basics)
- **Languages:** Python · Jekyll · HTML/Markdown · Familiar with C/C++, Fortran
- **Computer Misc.:** Linux · Wordpress/MAMP · git · BTTX · 3D-printing · Raspberry Pi

Publications

1. Laxmikant Pathade, Rahiem Davon Slaton, Tennyson Doane, Mathew M. Maye “Corrosion Resistance Performance of Fe/CrNi Core-Alloy Nanoparticles in Solution and as Thin-Films.” (To be submitted, 2018)
2. Laxmikant Pathade, Rahiem Davon Slaton, Tennyson Doane, Mathew M. Maye “Void Formation and Oxidation Resistance in FeNi Core/Alloy Nanoparticles.” (To be submitted, 2018)
3. Tennyson Doane, Laxmikant Pathade, Mathew M. Maye “Understanding Alloying and Phase Transformation in FeNi Core Alloy Nanoparticles at High Temperatures.” (To be submitted, 2018)
6. Tennyson Doane, Kayla Ryan, Laxmikant Pathade, Kevin Cruz, Huidong Zang, Mircea Cotlet, Mathew M. Maye “Using Perovskite Nanoparticles as Halide Reservoirs in Catalysis and as Spectrochemical Probes of Ions in Solution.” ACS Nano 2016, 10 (6), 5864–72 (doi: 10.1021/acsnano.6b0806)

Patents

**Selected Presentations**

- “Understanding the Oxidation Behavior of Stainless Transition Metal Core/Alloy Nanoparticles.” (Talk) Northeast Regional Meeting of the ACS, Binghamton, NY (2016)
- “Oxidation resistance interfaces in colloidal core/alloy nanoparticles” (Talk), ACS National Meeting, Philadelphia, PA (2016)
- “Oxidation behavior of stainless core/alloy nanoparticles” (Poster), ACS National Meeting, Philadelphia, PA (2016)
- “Corrosion Resistant Surfaces via Transition Metal Nanoparticle Chemistry” (Talk) Three Minute Thesis competition, Syracuse University (2016)
- “Synthesis and processing of core/alloy nanoparticles with stainless interfaces” (Poster), ACS National Meeting, Boston, MA (2015)
- “Synthesis and processing of core/alloy nanoparticles with stainless interfaces” (Talk), Northeast Regional Meeting of the ACS, Ithaca, NY (2015)
- “A solution to Industry defined problem: To recover coconut fatty acid monoethanolamine (MEA) from 3percent MEA mixture” (Talk), Young Innovators Choice Competition, ICT, Mumbai. (2012)
- “Synthesis and Applications of Color Formers” (Talk), ICT, Mumbai (2012)
- “Sorbitol & sorbitan esters, and their ethoxylated derivatives” (Talk), ICT, Mumbai (2012)

**Research Recognition**

  https://news.syr.edu/2016/05/chemists-add-color-to-chemical-reactions-81547/

**Honors and Awards**

- TA Mentor Award by the Graduate School at Syracuse University (Fall, 2016)
- Conference Travel Award, Department of Chemistry at Syracuse University (2015, 2016)
- Danve Family Foundation Award for Academic Excellence (2007, 2013)
- 2nd place Young Innovators’ Choice Competition at Institute of Chemical Technology (2012)
- Dow / Sudarshan Undergraduate Research Position (Summer REU) (2011)
- Ranked Regionally in National Science Olympiad, India (NSO-SOF) (2006)
- Navodaya Scholarship for 7 consecutive years (HRD Ministry, Govt. of India) (2002-2009)

**Professional Activities**

- **X-ray Facility Administrator** (2014-present)
  As a graduate facilities administrator, I run day-to-day operations of the powder X-ray diffractometer (Bruker D8-Advance) at the X-ray facility in the chemistry department at Syracuse University. Please refer work experience section for details.

- Peer reviewer for journals publishing in the field of Nanoscience.
  · Nanoscale (RSC) · Journal of Physical Chemistry (ACS) · Journal of Alloys and Compounds

- **Member of Professional Societies**
  American Chemical Society (ACS) · Material Research Society (MRS) · Society of Dyers and Colourists, India

**Outreach Activities & Services**

- Served as a special awards judge for ASM Material Education Foundation at the Central New York Science & Engineering Fair, SRC Arena at Onondaga Community College, Syracuse, NY (supported by Lockheed Martin, SRC Inc., Bristol-Myers Squibb, Saab, NASA, and the Technological Association of Central NY) (2017)
- volunteered at the Maker-hall event hosted by Technology Alliance of Central New York at the Annual Dr. MLK Jr. Community Celebrations, Nottingham High School, Syracuse, NY (2016)
- Student committee of the National Symposium on Functional Application of Colorants (NSFAC), held at ICT, Mumbai (2011 & 2012)