METAL NANOPlatelet SYNThesis AND DISPERSION IN SUSPENSION:
SILVER, COPPER, NICKEL AND RELATED ALLOYS

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ABSTRACT

The synthesis and dispersion of metal nanoplatelets were investigated in the current work, driven by the demands of miniaturization and low cost in the multilayer ceramic capacitor (MLCC) industry. The specific materials in this Ph.D. dissertation include silver (Ag), copper (Cu), nickel (Ni) and copper/nickel (Cu/Ni) metal platelets. Metal nanoplatelets were synthesized in the lamellar bilayer phase regime of the polyoxyethylene (POE) – water binary system. The main focus is on determining the processing parameters related to high yield platelet synthesis, laundering the nanoplatelets while maintaining well dispersed particles, and the dispersion approaches associated with interfacial and colloidal chemistry of specific metal systems.

A novel approach has been developed for the first time to statistically evaluate the morphology of the tabular shape nanoparticles using AFM analysis based on a relatively large population (n>200). The novel approach uses color delineation in the 3rd dimension (i.e., thickness) to produce both thickness and face diameter in the semi-automated analysis of several hundred nanoplatelets to quantify physical dimensions as well as to assess the degree of dispersion.

High yields of Ag nanoplatelets (20 g/liter) and Cu nanoplatelets (12 g/liter) were achieved in the POE-water bilayer system with controlled platelet morphology. The influence of higher concentrations of metal precursors on the presence of a lamellar phase in the POE-water binary phase diagram was investigated. Oxyethylene (EO)-water interactions decrease because of the influence of anion concentrations leading to dehydration of the POE head group. Phase separation was induced when the ion
concentration reached the upper limit. Therefore, the [water]/[surfactant] molar ratio used in the synthesis was decreased to compensate for the dehydration of the POE head groups to maintain the bilayer phase structure. In the Cu nanoplatelet synthesis, an elevated temperature was needed to increase the reaction rate. The free energy ($\Delta G_f$) of the oxyethylene (EO) / water structure is proportional to the number of EO units. As the temperature increased, the $\Delta G_f$ decreased, resulting in a favorable EO/EO interaction instead of an EO/water interaction. When the temperature reached the upper limit, phase separation occurred due to dehydration of water as the EO/water interactions become less favorable. Similarly as anion concentration increases, dehydration of the EO-head group causes collapse of the bilayer leading to phase separation. However, it is shown that so long as the bilayer structure is present even at relatively high anion concentrations, templated platelets are synthesized. Thus, the reasonably high yields are obtained for both the Ag-POE-water and Cu-POE-water syntheses.

A two-step protection-dispersion approach was investigated to stabilize Ag nanoplatelets in ethanol solution using a polyelectrolyte, polyethylenimine (PEI). As a cationic polyelectrolyte, degree of ionization of PEI is low at a high pH, and increases as pH decreases. To launder and concentrate Ag nanoplatelets without irreversible particle flocculation, PEI was used in initial washing iterations to form a protective polymer layer with a low charge. For the final wash, the solution pH was adjusted to provide a positive charge and promote electrosteric dispersion. The optimum PEI concentration and solution pH were investigated in ethanol. PEI self-aggregation behavior as a function of concentration and pH were examined. The PEI adsorption isotherm on silver was
established to quantitatively evaluate the adsorption between particle surface and the polyelectrolyte. It is shown that there is a range of pH values suitable for flocculation of the Ag nanoplatelets with PEI near the isoelectric point of the polymer, and a pH range for electrosteric dispersion of the Ag nanoplatelets defined at the lower pH, ~ pH 5.5, by PEI self-aggregation and at the higher limit, ~ pH 7.5, by PEI charge.

Prior to the dispersion study, the dispersion issues of Cu nanoplatelets in ethanol-water (7:3, vol%) are discussed, including dissolution, oxidation and possible surface charge heterogeneity. A passivation-dispersion approach was used to disperse Cu nanoplatelets in an ethanol-water (7:3, vol%) co-solvent. In this approach, a complexing agent is applied to the particle surface to form a stable surface metal-ligand complex with negligible Cu solubility in the solution. The formation of the stable complex is designed to protect against degradation, screen the possible charge heterogeneity in the solution, and provide a surface charge to promote reliable dispersion. Oxalic acid (HOx) and citric acid (HCit) were evaluated as dual passivation-dispersion agents. Colloid chemistry and surface chemistry were involved in evaluating the dispersion effectiveness. It was shown that HCit is an effective passivation-dispersion agent for stabilizing Cu nanoplatelets in an ethanol-water (7:3, vol%) co-solvent. At $10^{-3}$ M HCit concentration with respect to the solid loading, citrate provided a zeta potential equal to -25 mV, which was sufficient for dispersion. Sedimentation experiments and the electrostatic deposition technique verified that well-dispersed Cu nanoplatelet suspensions were obtained above pH 8.

Ni nanoplatelets were synthesized in POE-water bilayer system. To maintain POE-water self-assembled lamellar structure, synthesis temperature needs to be
controlled below \( \sim 60^\circ\text{C} \). With the temperature constraint, synthesis of pure phase Ni was conducted by the application of Pd as the nucleating agent at a molar ratio of \( 5 \times 10^{-2} \) Pd/Ni. \( \text{Cu}_{0.81}/\text{Ni}_{0.19} \) bimetallic nanoplatelets have also been synthesized in the same system using Cu as the nucleating agent.
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Chapter 1

Introduction

1.1 Statement of the Problem

Multilayer ceramic capacitors (MLCCs) have production and sales reaching 550 billion pieces and 6 billion dollars over the past 30 years.\(^1\) The average sales price for MLCCs is only 1.55 cents below that of other type of capacitors.\(^2\) Driven by the enormous market competition, the MLCC production industry cannot compete without continuing to focus on improved materials with lower cost, higher performance, improved reliability, and continued miniaturization.\(^2\)

MLCCs consist of alternating thin dielectric layers and internal electrode layers with external electrodes at the ends, as shown in Figure 1.1.\(^3\) Capacitance can be increased by decreasing the thickness of dielectric layers and increasing the number of layers.\(^4\) However, increasing the number of stacked dielectric layers sharply increases the proportion of the electrode cost to the overall cost. As a result, the cost of internal electrodes has become a greater part of the total cost. Up until 1995, most MLCCs were manufactured with expensive noble inner electrodes.\(^5\) Methods for reducing the internal electrode cost include\(^1\) (1) the use of Ag/Pd alloy electrodes with a high Ag content (more than 70 wt%) to achieve low-temperature sintering of the dielectrics or (2) the use of base metals, such as nickel (Ni) and copper (Cu), as internal electrodes which also requires the use of dielectric materials that can be fired in a reducing atmosphere.\(^6-9\) The
physical properties of various electrode materials for MLCCs are shown in Table 1.1. The development of base metal electrode (BME) played an important role in expanding the application of MLCCs.

![Schematic of a typical multilayer ceramic capacitor (MLCC). The three material systems of a MLCC are: dielectric, internal electrode and termination. Picture taken from ref. 3.](https://example.com/schematic)

**Figure 1.1.** Schematic of a typical multilayer ceramic capacitor (MLCC). The three material systems of a MLCC are: dielectric, internal electrode and termination. Picture taken from ref. 3.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Melting Point (°C)</th>
<th>Resistivity (mΩ)</th>
<th>Density (kg/m³)</th>
<th>Firing Atmosphere</th>
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**Table 1.1.** Physical properties of various electrodes materials for MLCC manufacture.¹
1.2 Particle Morphology Control

Since Faraday prepared gold sols of different colors in 1857\textsuperscript{10}, the preparation of metal colloids has been investigated, as these materials provided excellent models for studying the relationships between size, shape, and technologically have unique optical\textsuperscript{11}, electrical\textsuperscript{12},\textsuperscript{13} and magnetic properties\textsuperscript{14,15}.

Particle morphology control has generated increasing interest, because many material properties depend not only on their chemical composition, but also on particle size, shape and structure. Compared with traditional spherical nanoparticles, metal nanoplatelets with a thickness of a few nanometers have significant advantages through their improved surface coverage efficiency per unit area\textsuperscript{16}, better laydown ability for multilayers and coatings, and low roughness surfaces created by platelet films\textsuperscript{17}. Therefore, the first part of this project was the synthesis of silver, copper, nickel and copper/nickel nanoplatelets and the scaling up of the synthesis yield for the application to MLCCs fabrication.

Growth directed syntheses and template directed synthesis\textsuperscript{18} are widely used to control particle morphology. Growth directed synthesis is based on the use of specific growth directing agents\textsuperscript{18}. Bell and Adair\textsuperscript{19} have shown that the use of specific adsorbates can control the morphology of alpha-alumina precipitated from a glycol solution. The typical shapes were plate-like, but spindle-shaped alpha-alumina particles were also produced in the presence of acetic acid. Kandori et al.\textsuperscript{20} demonstrated that a variety of particle morphologies could be produced with dimethylformamide (DMF). It was shown that the morphology of hematite particles changed from spherical to
prismatic-shaped as DMF concentration increased. Goia and Matijević\textsuperscript{21} have provided a rather comprehensive review of the preparation of monodispersed metal particles, which documents many synthesis conditions for a number of important metal systems, including Pd, Cu, and Fe.

The use of self-assembly systems as templates has gained much attention in recent years, wherein the growth is directed via a pre-existing structure upon which nucleation and growth take place.\textsuperscript{22-24} A comprehensive review written by Osseo-Asare\textsuperscript{25} compiles the many materials and conditions used to synthesize metal oxides. Most of these particles are of nanometer size because of the nature of water-in-oil structures in the aqueous nano-reactors provided by self-assembled systems. Table 1.2 presents relevant metal nanoplatelets (Ag, Cu and Ni) synthesized in self-assembled systems.

Table 1.2. Selected metal nanoplatelets (Ag, Cu and Ni) synthesized in microemulsion systems.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reactants</th>
<th>Microemulsion System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>AgNO\textsubscript{3}</td>
<td>Octylamine-water\textsuperscript{16}</td>
</tr>
<tr>
<td></td>
<td>Ag(AOT)</td>
<td>C\textsubscript{12}E\textsubscript{4}-water\textsuperscript{26}</td>
</tr>
<tr>
<td>Cu</td>
<td>CuSO\textsubscript{4}</td>
<td>Ag(AOT)-Na(AOT)\textsuperscript{27}</td>
</tr>
<tr>
<td>Ni</td>
<td>NiCl\textsubscript{2}</td>
<td>Cu(AOT)\textsubscript{2}-Na(AOT)-water-isoctane\textsuperscript{28}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Octylamine-water\textsuperscript{17}</td>
</tr>
</tbody>
</table>
Table 1.3. Guidelines for the selection of reducing agents and the reaction conditions in the precipitation of various metal particles. The reduction conditions listed are applicable only to uncomplexed metal ions. Table taken from ref. 21.

<table>
<thead>
<tr>
<th>Metal Species</th>
<th>$E^\circ$ (V)</th>
<th>Reducing Agent</th>
<th>Conditions</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Au^{3+,+}$, $Pt^{4+,2+}$, $Pd^{2+}$</td>
<td>$\geq +0.7$</td>
<td>Organic acids, alcohols, polyols</td>
<td>$\geq 70^\circ$C</td>
<td>Slow</td>
</tr>
<tr>
<td>$Ag^+$, $Rh^{3+}$, $Hg^{2+}$, $Ir^{3+}$</td>
<td></td>
<td>Aldehydes, sugars</td>
<td>$&lt; 50^\circ$C</td>
<td>Moderate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrazine, $H_2SO_3$, $H_3PO_2$</td>
<td>Ambient</td>
<td>Fast</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$NaBH_4$, boranes, hydrated e$^-$</td>
<td>Ambient</td>
<td>Very fast</td>
</tr>
<tr>
<td>$Cu^{2+}$, $Re^{3+}$, $Ru^{3+}$</td>
<td>$&lt; 0.7$ and $\geq 0$</td>
<td>Polyols</td>
<td>$&gt;120^\circ$C</td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aldehydes, sugars</td>
<td>70-100$^\circ$C</td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrazine, hydrogen</td>
<td>$&lt;70^\circ$C</td>
<td>Moderate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$NaBH_4$</td>
<td>Ambient</td>
<td>Fast</td>
</tr>
<tr>
<td>$Cd^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Fe^{2+,3+}$</td>
<td>$&lt; 0$ and $\geq -0.5$</td>
<td>Polyols</td>
<td>$&gt; 180^\circ$C</td>
<td>Slow</td>
</tr>
<tr>
<td>$In^{3+}$, $Sn^{2+}$, $Mo^{3+}$, $W^{6+}$</td>
<td></td>
<td>Hydrazine, hydroxylamine</td>
<td>70-100$^\circ$C</td>
<td>Slow</td>
</tr>
<tr>
<td>$Cr^{3+}$, $Mn^{2+}$, $Ta^{5+}$, $V^{2+}$</td>
<td>$&lt; -0.6$</td>
<td>$NaBH_4$, boranes</td>
<td>Ambient</td>
<td>Fast</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrated e$^-$, radicals</td>
<td>$T$, $P&gt;\text{ambient}$</td>
<td>Slow</td>
</tr>
</tbody>
</table>

$E^\circ$ is the standard half cell reduction potential for metal ions reduced to the metal.
1.3 Formation Mechanisms

In a liquid medium, the formation of metal atoms is due to the transfer of electrons from a reducing agent to the oxidized metallic species. The driving force of the electron transfer is the standard redox potential \( E_{\text{cell}}^{\circ} \) of the two half cell reactions. The increase in \( E_{\text{cell}}^{\circ} \) results in a more rapid generation of atoms in the liquid, leading to a faster nucleation. Goia et al. provided the guidelines for selecting reducing agents and working conditions listed in Table 1.3. Electron transfer gradually forms small clusters called embryos, given by Eq. (1.1)

\[
x\text{Me}^{\circ} = (\text{Me}^{\circ})_{\text{em}}
\]

As new metal atoms are formed in the system, the embryos that reach a critical size and separate from the solution can form nuclei. \( \text{(Me}^{\circ})_{\text{em}} + y\text{Me}^{\circ} = (\text{Me}^{\circ})_{\text{nucl}} \)

The number and size of the nuclei generated in the solution are related to the redox potential, temperature, concentration of the surfactant, and other physical chemical factors. The nuclei lead to the formation of primary particles by diffusional growth. Depending on the experimental conditions, the primary particles can form larger crystalline materials by diffusion, as suggested by LaMer and Dinegar. Ostwald ripening may also affect particle growth, in which the smaller particles dissolve and larger ones grow. The driving force for the coarsening in Ostwald ripening is the reduction of the interfacial free energy.
1.4 Self-Assembly Molecular Structure

Self-assembly systems have great potential to synthesize anisotropically-shaped particles. Molecular self-assembly is a spontaneous association of amphiphiles into structurally stable, well-defined micellular structures under equilibrium conditions. The associated self-assembled structures have a minimum surface free energy for their size and shape. The surface energy is dictated by factors such as repulsive forces from the head group, hydrophobic attraction of hydrocarbon chain line, interaction between aggregates at high surfactant concentrations, and relative size and shape of polar and hydrophobic parts of the amphiphiles.

In the current work, lamellar bilayers have been used as a template for the synthesis of tabular nanoparticles. A lamellar bilayer phase consists of alternating parallel planes of bilayers separated by intercalated layers of a solvent, usually water. The surfactant in the bilayer structure is arranged with the hydrophilic portions of the molecules in contact with the aqueous layer, and the hydrophobic tails of the molecules at the center of the lamellae. The aqueous layers act as domains for the nucleation and growth of platelet particles.

The octylamine-water bilayer system was used to synthesize silver, nickel and silver/palladium nanoplatelets by Yener et al.. Figure 1.2 shows the binary phase diagram of octylamine-water system. The marked area indicates the bilayer phase region where synthesis took place by Yener et al.. At room temperature, the bilayer phase exists in a range from 45 wt% to 70 wt% octylamine. Bilayer phase separation occurs for temperatures above 35°C. Furthermore, octylamine is highly alkaline (~ pH 13), the
previous work by Yener et al.\textsuperscript{17} showed that to disperse Ag nanoplatelets particles using polyethylenimine (PEI) as an effective polyelectrolyte required a large amount of acetic acid to decrease the suspension pH to ~ pH 6. The addition of acetic acid increases the ionic strength of the silver suspension resulting in double layer compression leading to agglomeration of the silver nanoplatelets in ethanol.

Figure 1.2. Binary phase diagram of octylamine water system.\textsuperscript{38} Shaded region indicates the laminar bilayer phase stability region.
In the current synthesis work, polyoxyethylene (POE)-water system was used as an alternative to the octylamine-water bilayer system. POE is a nonionic surfactant with an autogenous value of pH 7. It will be demonstrated that PEI is as an effective dispersant at ~pH 6.5, no need to introduce acid to adjust pH, avoiding the high ionic strength issue inherent to the octylamine-water system. In addition, the POE-water system has the ability to form bilayers over a wide range of concentrations at 25°C as illustrated by the $L_\alpha$ (lamellar bilayer) phase region in phase diagram, as shown in Figure 1.3. There is no bilayer phase separation below 70°C promoting synthetic pathway ways for base metal platelets (that is, copper and nickel nanoplatelets) through increasing temperature to stimulate the kinetics of reduction. However, the nature of water/oxyethylene (EO) interactions undergoes a critical change with increasing temperature. Mitchell et al.\textsuperscript{39} proposed the existence of “structured water” around the EO chain at a critical EO: water ratio, which strongly depends on the temperature. The free energy of formation ($\Delta G_f$) of this structure is expected to be proportional to the number of oxyethylene units. As the temperature increases, the $\Delta G_f$ decreases which results in a favorable EO/EO interaction instead of an EO/water interaction collapsing the self-assembly structure. Thus increases in temperature can induce phase separation due to the dehydration of water from the POE head group region, as water/EO interactions became less energetically favorable.
1.5 Colloidal Stabilization Mechanisms

By controlling the interparticle forces, colloidal suspensions can be categorized into three main states: dispersed, weakly flocculated or strongly flocculated, as illustrated in Figure 1.4. Colloidal stability is governed by the total interparticle potential energy, which involves at least three main types of interaction: (1) the London-van der Waals attraction force; (2) the Coulombic (repulsive or attractive) force associated with charged particles; and (3) the repulsive force resulting from adsorbed layers. Three types
of colloidal stability related to various combinations of these forces will be discussed, as illustrated in Figure 1.5.

![Figure 1.4. Schematic diagram of the colloid suspension states showing three categories: dispersed, weakly flocculated, and strongly flocculated. Picture modified from ref. 41.](image)

The attractive potential energy resulting from long-range van der Waals interactions among particles and the repulsion potential energy due to electrostatic interaction between like-charged particle surfaces (Figure 1.5A) form the well-known Derjaguin-Landau-Verwey-Overbeek (DLVO)\textsuperscript{43, 44} theory. The attractive force between solid particles can be calculated based on the assumption of Hamaker that the interactions between individual atoms or molecules are additive, so therefore integrating over all for two interaction particles of them leads to the total energy. The attractive potential
energy, $V_A$, between two semi-infinite flat plates as a function of separation distance ($D$) is given by Eq. (1.3)\(^{45}\)

$$V_A(D) = -\frac{A_{131}}{12\pi D^2}$$

where $A_{131}$ is the Hamaker constant of particle 1 in a medium 3. The higher the Hamaker constant, the stronger the van der Waals attraction forces between particles.

There are two methods of calculating the Hamaker constant between solids.\(^{46}\) The first is the microscopic approach\(^{47}, 48\) which calculates van der Waals force by integration over all pairs of atoms and molecules as developed by Hamaker. The second is the macroscopic approach developed by Lifshitz,\(^{49}\) which is physically more satisfactory.\(^{46}\)
Figure 1.5. Schematics of three types of particle interaction in colloidal stabilization. (A) Electrostatic stabilization resulting from the interaction of two like-charged particles. (B) Steric stabilization due to the interaction of adsorbed polymers that provide steric hindrance between particle surfaces. (C) Electrosteric stabilization resulting from the interaction of charged polymer layers with the particle. Picture drawn by Adair JH.
The macroscopic approach starts from the optical properties of the interacting macroscopic bodies and calculates van der Waals attraction from the imaginary parts of their complex dielectric constants, especially the far ultraviolet portions.\textsuperscript{46} The key aspect of the Lifshitz theory is that the intermolecular attraction between particles expressed by Hamaker constant can be described by the dispersion of the dielectric constant of the materials of interest. A number of calculation methods can be used to experimentally or theoretically determine Hamaker constants, including the Gregory approximation, Eq. (1.4),\textsuperscript{50} and the Tabor-Winterton approach, Eq. (1.5)\textsuperscript{51}.

\[
A_{11} = \frac{0.230 h \nu_v (\varepsilon_\infty - 1)^2}{(\varepsilon_\infty + 1)^3 (\varepsilon_\infty + 2)^3} \tag{1.4}
\]

where \( h \) is the Planck constant, \( \nu_v \) is the characteristic dispersion frequency and \( \varepsilon_\infty \) is limiting dielectric constant.

\[
A_{131} = \frac{3}{4} K T \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 + \frac{3 h \sigma_e}{16 \sqrt{2}} \left( \frac{n_1^2 - n_3^2}{n_1^2 + n_3^2} \right)^3 \tag{1.5}
\]

where \( A_{131} \) is the Hamaker constant for two identical materials 1 interacting across a medium 3, \( \varepsilon_1 \) and \( \varepsilon_3 \) are the dielectric constants of materials and medium, \( n_1 \) and \( n_3 \) are the refractive indexes of materials and medium respectively, and \( \sigma_e \) is the electronic relaxation frequency.

As predicted by the DLVO theory, repulsion between two particles can be controlled by generating like-charges on the particle surfaces.\textsuperscript{41} The charge on a particle surface attracts counter-ions chemically bonded to the particle surface known as the Stern
layer, as shown in Figure 1.6. The potential difference between the Stern plane and the bulk liquid is denoted the zeta potential ($\zeta$), and its magnitude indicates the charge magnitude in the counter ion layer to achieve electroneutrality for the particle and surrounding liquid. The ions further away from the core particle make up a diffuse, loosely bound layer called Gouy-Chapman Layer. The extension of the Gouy-Chapman layer governs the electrostatic repulsion arising from overlapping Gouy-Chapman layers. The resulting system of a surface charge and a corresponding counter-charge on the liquid side of the interface is denoted as the electric double layer.

![Diagram of the electrical double layer](image)

**Figure 1.6.** The electrical double layer at a negatively charge surface with a Stern layer of positive ions adsorbed to the surface. $\Psi_0$ and $\Psi_S$ are the potential at the particle surface and the Stern layer, respectively. The potential between the stern plane and the bulk liquid is denoted the zeta potential ($\zeta$). Picture taken from ref. 52.
The Debye-Hückel parameter, $\kappa$, is the inverse thickness of the double layer, given by Eq. (1.6)\cite{16}

$$
\kappa = \sqrt{\frac{F^2 \sum_i c_i z_i^2}{\varepsilon_r \varepsilon_0 k T}}
$$

(1.6)

where $c_i$ and $z_i$ are the number density and valence of the counter-ions of type $i$, $\varepsilon_r$ is the relative permittivity, and $F$ is the Faraday constant. The Debye-Hückel parameter plays a prominent role in double layer theory. Decreasing the Gouy-Chapman layer thickness causes the repulsive potential to decrease. Therefore, as $\kappa$ increases, the tendency for aggregation increases. The ionic strength ($I$), given by Eq. (1.7)\cite{53} can also influence the surface potential. Increasing ionic strength compresses the Gouy-Chapman layer, causing the repulsive potential to decrease more rapidly as the distance from the particle surface increases.

$$
I = \frac{\sum_{i=1}^{m} c_i z_i^2}{2}
$$

(1.7)

where $m$ is the number of ionic species, $c_i$ is the concentration of species type $i$, and $z_i$ is the valence of species $i$. The tendency for aggregation increases as $I$ increases. In conclusion, increasing ionic strength causes an increase in $\kappa$ as a result of which the electric potential in the Gouy-Chapman layer falls off more rapidly with distance. This is known as “compression of the double layer”.\cite{53}
In steric stabilization (Figure 1.5B), adsorbed polymeric molecules are utilized to induce steric repulsion. The steric repulsion is combined with an osmotic repulsion at relatively large separation distance, \(2L\), where \(L = 2R_g\), \(R_g\) is the radius of gyration of free polymer in the bulk solution. At separation distances less than \(2L\), true steric repulsion due to interpenetrating polymer chains leads to the repulsive forces between two interacting surfaces. To overcome the van der Waals attraction and to prevent bridging flocculation, the adsorbed layers must be of sufficient thickness and density. The conformation of adsorbed polymer layers can vary depending on solvent quality, molecular architecture, and colloid and organic concentrations. de Gennes used scaling laws for adsorbed polymer interaction to predict repulsive energy for two interacting particles as a function of adsorption density and thickness of the adsorbed layers.

Electrosteric stabilization (Figure 1.5C) provides an alternative route to stabilize colloidal suspension by a combination of electrostatic and steric interaction. Polyelectrolyte species contain at least one type of ionized group with molecular architectures ranging from homopolymers to block copolymers. Polyelectrolyte adsorption is ultimately associated with the chemical and physical properties of the solid surfaces and solvent medium. Furthermore, adsorption is greatly favored by electrostatic attraction when the polyelectrolyte carries opposite charges to that of the particle surface. At a low adsorption concentration, such species can promote flocculation via surface charge neutralization, bridging or charge-patch mechanisms. At higher adsorption coverage, long-range repulsive forces due to the electrosteric interactions promote suspension stability.
1.6 Objectives of Research

The specific objective of this research was to investigate the role of colloidal chemistry in controlling particle morphology and the laundering/dispersion behavior of metal nanoplatelets in suspension. To accomplish this goal, silver, copper, nickel and copper/nickel nanoplatelets were synthesized via a self-assembled bilayer structure. Colloidal metal nanoplatelets were recovered in a well-dispersed state through the protection-dispersion and passivation-dispersion approaches. The further objectives of this dissertation comprised five major sections.

Chapter Two summarizes the basic principles of the main characterization techniques used in the current work.

For Chapter Three, tabular shaped silver (Ag) nanoparticles with uniform size distribution were synthesized in a polyoxyethylene (POE) / water bilayer system. A protection-dispersion approach was established to stabilize Ag nanoplatelets in ethanol using polyethylenimine (PEI). Well-dispersed Ag nanoplatelets were obtained by the two-step method with the state of dispersion assessed using quasi-elastic light scattering (QELS), and zeta potential measurements. A novel approach was also developed to statistically evaluate the morphology of the tabular shaped nanoparticles using AFM analysis based on a relatively large population (n>200). This approach uses color delineation in the 3rd dimension (i.e. thickness) to determine both thickness and face diameter in the semi-automated analysis of several hundred nanoplatelets in order to quantify physical dimensions as well as to assess the degree of dispersion.
Chapter Four focuses on the high yield synthesis (20 grams / liter) of silver (Ag) nanoplatelets in a POE-water bilayer system. The presence of the lamellar bilayer phase in the binary POE-water phase diagram was investigated as a function of the concentrations of silver precursor. The adsorption behavior of PEI on the surface of Ag nanoplatelets was examined and discussed based on the surface chemistry of Ag and PEI in an ethanol solution.

Chapters Five and Six focus on the synthesis and dispersion of copper nanoplatelets. In Chapter Five, Cu nanoplatelets were efficiently prepared in a POE-water bilayer system by increasing temperature. The higher degree of supersaturation led to a uniform particle morphology. A three-stage oxidation due to the particle morphology is discussed based on thermal analysis experiments. In Chapter Six, the critical issues associated with the dispersion of Cu nanoplatelets are addressed. A well-dispersed Cu nanoplatelet suspension was achieved in an ethanol-water (7:3, vol%) co-solvent through a passivation-dispersion approach. Oxalic acid (HOx) and citric acid (HCit) were investigated as the passivation-dispersion agents. The solution chemistry (dispersant concentration, conductivity, ionic strength, etc.) was investigated to optimize the dispersion parameters.

Chapter Seven covers the synthesis of nickel and copper/nickel nano-alloys in a POE-water self-assembly bilayer system. An increase in nuclei density was achieved with the use of nucleating catalysts. Cu, Pd and Ag were investigated as nucleating catalysts.

Chapter Eight outlines the conclusions and suggested future work drawn from the developments of the current work.
1.7 References


Chapter 2

Characterization Techniques: Basic Principles

2.1 Introduction

Nanoscience and nanotechnology involve three key steps: first, the synthesis of size- and shape-controlled nanoparticles; second, the characterization of nanoparticles aimed at understanding, controlling and designing new nanomaterial systems; and third, the development of new devices using nanomaterials.

This chapter emphasizes the main techniques used for characterizing nanophase materials in the current work. The basic principles of each technique were briefly described, including atomic force microscopy (AFM), transmission electron microscopy (TEM), quasi-elastic light scattering (QELS) for hydrodynamic diameter measurement, X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis), thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), phase analysis light scattering (PALS) for zeta potential measurement, specific surface area measurement by gas adsorption method and related computer programs used in the current work.

2.2 Atomic Force Microscopy (AFM)

Invented by Binnig et al., the atomic force microscope (AFM) has been used to image both conductors and insulators with a lateral resolution of 3 nm, a vertical resolution of less than 0.1 nm, and surfaces with relatively low surface roughness (less
than 5.5 μm maximum z-axis height). Height measurements in an AFM require that the piezoelectric ceramics in the Z axis of the microscope are linear and calibrated.

The AFM utilizes the principles of scanning tunneling microscopy (STM) and the stylus profilometer to measure the force between the tip and the surface. Force can be measured in air, vacuum and liquid media. Figure 2.1 shows a schematic diagram of the basic setup. An AFM sample is mounted on a piezoelectric scanner, which moves the sample in three dimensions, while a flexible cantilever with a sharp tip is held in place above the sample surface. A laser beam is reflected off the back of the cantilever into a position sensitive detector. From the contact between the tip and the sample surface, changes in the deflection of the tip are registered by the movement of the laser on the position sensitive detector. Feedback electronics is designed to keep the tip and sample interaction constant.

![Figure 2.1. Schematic diagram of atomic force microscopy (AFM). AFM hardware typically has four basic elements including: a probe (cantilever and tip), a scanner, detection mechanism, and feedback electronics. The picture has been modified from ref. 4.](image-url)
**Tapping Mode™ imaging.** Tapping Mode™ imaging is typically used for delicate samples, such as biological samples and samples at a nanometer scale which might be distorted or damaged by the tip sliding across the surface. Tapping Mode™ inherently overcomes problems associated with the friction and adhesion that occurs in conventional contact mode imaging. Tapping Mode™ imaging is implemented by oscillating the cantilever assembly at or near the cantilever's natural resonance frequency while allowing the cantilever tip to impact the sample for a minimal amount of time. When the tip is not in contact with the sample surface, the piezo motion causes the cantilever to oscillate at amplitudes typically greater than 20 nm. The oscillating tip is then moved toward the sample until it lightly touches, or taps, the surface. During scanning, the oscillating tip vertically contacts the surface and lifts off with a frequency of 50,000 to 500,000 cycles per second. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is reduced due to the energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to measure surface features.

In Tapping Mode™, the cantilever oscillation amplitude is kept constant by a feedback loop. The optimal oscillation frequency is automatically selected by the software and the force on the sample is automatically maintained at the lowest level. In addition, the surface is not forced sideways since the applied force is always vertical. When the tip contacts the sample, the high frequency (50 k – 500 k Hz) makes the surface viscoelastic, and the adhesion force between the tip and the sample is greatly reduced. When the tip passes over a bump in the surface, the cantilever oscillates less and the amplitude of oscillation decreases. Likewise, when the tip passes over a depression, the
oscillation and the amplitude of the cantilever increase. The tip’s oscillation amplitude is measured by the detector and recorded by NanoScope III controller electronics. An AFM image of Ag nanoplatelets using Tapping Mode™ is shown in Figure 2.2.

Figure 2.2. AFM topography image (upper left) and amplitude image (upper right) of Ag nanoplatelets. The section analysis (lower left) shows that the Ag nanoplatelets had an average face diameter of 40 ± 2 nm and an average thickness of 8 ± 1 nm (± 95% confidence interval, n = 5, sample No. YY1-5). The Ag nanoplatelets were synthesized in a polyoxyethylene-water bilayer system in the current work. The sample was prepared by placing drops of the ethanolic Ag nanoplatelet suspension on atomically flat, freshly cleaved mica and dried at 350°C in air.
When used in fluid, Tapping Mode™ can image surfaces with high resolution. However, imaging in a liquid medium tends to damp the cantilever's normal resonant frequency. Therefore, the entire fluid cell can be oscillated to drive the cantilever into oscillation. This is different from Tapping Mode™ or a non-contact mode in air or a vacuum, where the cantilever itself is oscillating. At an appropriate frequency, typically between 5,000 and 40,000 cycles per second, the amplitude of the cantilever decreases when the tip begins to tap the sample.

In the current work, section analysis is most commonly used to reveal the profile of the surface according to the topography of the sample. It provides the most useful measurements of surface features, including vertical distance, horizontal distance, roughness along section lines, etc. Roughness analysis has also been used in this work, and it generates a wide variety of statistics including the vertical difference between the highest and lowest points (Z range) and the root mean square ($R_g$). $R_g$ is given by Eq. (2.1)

$$R_g = \sqrt{\frac{\sum_{i=1}^{N} (Z_i - Z_{ave})^2}{N}}$$  \hspace{1cm} (2.1)

where $Z_{ave}$ is the average height value within the given area, $Z_i$ is the current height value, and $N$ is the number of points within the given area. Average roughness ($R_a$) is the arithmetic average of the absolute values of the surface height deviations measured from the mean plane, given by Eq. (2.2)

$$R_a = \frac{1}{N} \sum_{j=1}^{N} |Z_j|$$  \hspace{1cm} (2.2)
2.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) characterizes materials down to their atomic limits with its high lateral spatial resolution (better than 0.2 nm), and has outstanding ability to provide structural, phase and crystallographic information.\textsuperscript{10}

In TEM, a focused electron beam is incident on a thin specimen with a thickness less than 200 nm.\textsuperscript{4} A schematic diagram of a TEM instrument is illustrated in Figure \ref{fig:2.3}, showing the location of the specimen and the principle lenses within the TEM column.

**Bright field (BF) / Dark field (DF) image modes.** The two basic operations of forming a bright field image and a dark field image are illustrated in Figure \ref{fig:2.4}. To form an image, the intermediate lens is adjusted so that the objective plane is the image plane of the objective lens. The image is passed through the intermediate and projector lenses while being magnified.\textsuperscript{10} In bright field (BF) imaging, an aperture is placed so that it blocks the entire diffraction pattern and only passes the transmitted (non-diffracted) electron beam.

Several mechanisms can create contrast in images.\textsuperscript{10} One is mass contrast, which is primarily due to incoherent elastic scattering; spatial separations between scattering centers are not periodic. Another mechanism is thickness contrast, which results from nonuniformity in the thickness of the sample. When thickness or compositional variations, or structural anomalies are present, electrons in some areas are scattered out of
Figure 2.3. Schematic diagram of a TEM instrument. An image is formed, magnified and delivered by magnetic lenses above and below the sample on a fluorescent screen, a layer of photographic film or a charge coupled device (CCD) camera. Picture taken from ref. 4.
Figure 2.4. Two basic operations of the TEM imaging system: bright-field imaging (left) and dark-field imaging (right). When the aperture is inserted to pass only the transmitted electrons, a bright-field image is formed. When the aperture is placed to pass only some diffracted electrons, a dark-field image is formed. Picture taken from ref. 11.
the primary beam to a greater extent than in neighboring regions. A third mechanism is
diffraction contrast, which results from coherent elastic scattering - coherent because of
the periodic scattering arrangement in crystalline materials. Diffraction contrast is often
obtained in the vicinity of defects in the lattice. When the aperture passes only some of
the diffracted electrons, a dark-field image is formed.11

High resolution image mode (HRTEM). High resolution (HR) TEM uses not
only the transmitted beam, but also at least one diffracted beam. All of the beams are
recombined in the image-forming process, preserving their amplitudes and phases. In
high-magnification, it is possible to see what is called phase contrast in the form of
periodic fringes, which represent the direct resolution of the Bragg reflecting planes. The
HRTEM has gained popularity with the availability of high-voltage TEMs with spatial
resolutions in excess of 0.2 nm.10 Figure 2.5 shows an HRTEM image of a Cu
nanoplatelets synthesized in the current work (for synthesis details see Chapter 5).

Selected area diffraction (SAD). Diffraction patterns provide information on
crystallography. In TEM, a single crystal produces a spot pattern, a polycrystal produces
a ring pattern, which is a superposition of diffraction patterns from crystallites, and a
glassy or amorphous material produces a series of diffuse halos.10

A ray diagram for obtaining a diffraction pattern is illustrated in Figure 2.6.11 In
the SAD operation, the sample is first observed in image mode until a region of interest is
found. Then a specific area of the sample is selected to contribute to the diffraction and
to reduce the intensity of the pattern.10 The standard method is to insert a selecting
aperture above the specimen, which permits electrons that pass through it to hit the
sample. In this method, a diffraction pattern is obtained with a parallel electron beam and
Figure 2.5. HRTEM micrograph of Cu nanoplatelet shows the presence of an amorphous oxide layer with a thickness of ~ 3 nm due to the corrosion of Cu\(^{2+}\) on particle surface. The Cu nanoplatelets were synthesized in a polyoxyethylene-water bilayer system at 55°C and treated in an ethanol-water (7:3, vol%) co-solvent in the current work.
Figure 2.6. Schematic diagram of selected area diffraction (SAD) mode. The dashed lines and arrows indicate that the intermediate lens is focused on the back focal plane of the objective lens. The transmitted beam and diffracted beams are imaged. The SAD aperture is inserted in the image plane of the objective lens to confine the diffraction pattern to a selected area of the specimen. Picture modified from ref. 11.
this is called selected area diffraction (SAD) and was invented by LePoole.\textsuperscript{12} The SAD pattern is projected on the viewing screen with a fixed camera length ($L$), which is the distance of the film from the diffraction pattern\textsuperscript{10}.

The separation of the diffraction spots can be used to determine interplanar spacing in crystals\textsuperscript{11}. As illustrated in Figure 2.7, the interplanar spacing, $d$, can be determined by measuring the separation distance, $r$, between diffraction spots. When $\theta$ is $\sim 1^\circ$ for low order ($n=1$) diffractions by Eq. (2.3)$\textsuperscript{10}$

$$\frac{r}{L} = \tan (2 \theta) \sim 2 \theta \quad (\theta \leq 1^\circ) \quad (2.3)$$

From the Bragg equation, Eq. (2.4)$\textsuperscript{13}$, the interplanar spacing, $d$, is given in Eq. (2.5)$\textsuperscript{11}$

$$\frac{\lambda}{d} = 2 \sin \theta \sim 2 \theta \quad (\theta \leq 1^\circ) \quad (2.4)$$

$$rd = \lambda L \quad (2.5)$$

![Figure 2.7](image_url)  

Figure 2.7. Geometry for electron diffraction and definition of camera length ($L$). This permits a determination of interplanar spacing, $d$, by measuring the separation of diffraction spots, $r$. When Bragg’s law is combined with the above geometry, $d$ can be calculated using $rd = \lambda L$. ref. 11.
2.4 Dynamic (Quasi-Elastic) Light Scattering or Photon Correlation Spectroscopy (DLS, QELS or PCS)

This procedure relies on the fact that when a light photon hits a moving particle, the frequency of the scattered light will be different from the incident frequency. The frequency increases slightly when the particle is moving towards the observer and decreases when the particle is moving away from the observer. This is called Doppler broadening and it provides a means of determining the diffusion coefficient of the particles. The intensity, $I$, of the scattered light of frequency, $\omega$, can be represented by Eq. (2.6)\textsuperscript{14}

$$I(\omega) = A_1 \frac{DQ^2}{(\omega - \omega_0)^2 + (DQ^2)^2}$$  \hspace{1cm} (2.6)

where $D$ is the diffusion coefficient, $\omega_0$ is the frequency of the incident radiation, $A_1$ is a constant, and $Q$ is the magnitude of the scattering vector at a specific angle, $\theta$, given by Eq. (2.7)\textsuperscript{15}

$$Q = \left( \frac{4\pi n_0}{\lambda_0} \right) \sin \left( \frac{\theta}{2} \right)$$  \hspace{1cm} (2.7)

where $n_0$ is the refractive index of the medium and $\theta$ is the scattering angle. $Q$ corresponds to how strongly the light interacts with the particles. The intensity of the signal is given by Eq.(2.5), from which $[D]$ and consequently a mean radius, $a$, can be calculated using the Einstein Eq. (2.8)\textsuperscript{16}

$$D = \frac{k_BT}{B}$$  \hspace{1cm} (2.8)
where $k_B$ is Boltzmann’s constant, $T$ is the temperature and $B$ can be derived from Stokes Eq. (2.9)\textsuperscript{16}

$$B = 6\pi\eta a$$  \hspace{1cm} (2.9)

where $\eta$ is the viscosity of the fluid. Therefore, $a$ can be calculated by the Stokes-Einstein Eq. (2.10)\textsuperscript{16}

$$a = \frac{k_B T}{6\pi\eta D}$$  \hspace{1cm} (2.10)

Analysis of the time dependence of the intensity fluctuation yields the diffusion coefficient of the particles. Via the Stokes-Einstein equation, the viscosity of the medium, the hydrodynamic radius, or the diameter of the particles can be calculated. Dynamic light scattering is particularly suited for determining small changes in mean diameter, such as those that result from adsorbed layers on the particle surface or slight variations in manufacturing processes.\textsuperscript{17} Using a coherent and monochromatic laser source makes it possible to observe time-dependent fluctuations in the scattered intensity through a suitable detector, such as a photomultiplier capable of operating in photon counting mode.

Figure 2.8 shows a commercial Malvern dynamic light scattering system with a detection limit from 3 nm to 10 $\mu$m.\textsuperscript{18} A laser illuminates the sample cell. For diluted concentrations, most of the laser beam passes through the sample cell, but some is scattered by the particles at all angles. A backscattered detector is positioned at 173$^\circ$ to measure the scattered light, which also has no contact with the sample and hence is called non-invasive. There are two advantages to non-invasive backscattered detection. First,
the laser does not travel through the entire sample to reduce multiple scattering, where light from one particle is itself scattered by other particles. Second, since the light passes through a shorter path of the sample, higher concentrations can be measured.

The intensity of the scattered light must be within a specific range for successful detection. To optimize the intensity, an attenuator, positioned between the laser source and the sample cell, is applied. If too much light is detected, the detector will be saturated. In this case, the attenuator reduces the intensity of the laser source and therefore reduces the scattered light. On the other hand, for samples with small particle size or of low concentrations, the amount of scattered light needs to be increased, so the attenuator allows more laser light to pass through the sample. The appropriate attenuator position is automatically determined by the built-in software and covers a transmission range from 100 % to 0.0003 %.

Figure 2.8. Optical configuration of particle size measurement based on quasi-elastic light scattering. A Zetasizer Nano S was used for the particle size distribution measurement in the current work. Picture redrawn from ref. 18.
The scattering intensity from the detector is passed to a digital processing board called a correlator, which compares the scattering intensity at successive time intervals to derive its varying rate. The correlator information is then passed to a computer to derive size information. As an example, the particle size distribution of gold nano-colloids measured by a Zetasizer Nano S (Malvern Instrument Ltd. England) is shown in Figure 2.9.

Figure 2.9. Hydrodynamic diameter distribution (number%) of well-dispersed gold nanoparticles measured by quasi-elastic light scattering using a Malvern Zetasizer. Gold nanoparticles were synthesized by a method adapted from Hauser and Lynn.19 The gold nanoparticles were spherical in shape with an average particle size of ~17 nm, which was used for evaluating the charge heterogeneity of Cu nanoplatelets in the current work (for details see Chapter 6).
2.5 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) can be used to identify the crystalline phases in materials and to analyze structural properties such as stress, grain size, phase composition, crystal orientation and defects in the present phases.\(^4\) XRD can be performed in most environments and therefore can be used for preliminary materials phase characterization. Typical trace capability of XRD analysis is ~ 3 atomic percent in a two phase mixture.\(^4\)

Figure 2.10. Schematic diagrams of crystalline material diffract x-rays according to Bragg’s law: a typical XRD experiment set up (left), several atomic planes and their \(d\)-spacing in a simple cubic crystal (upper right) and Miller indices of atomic planes in a simple cubic crystal (lower right). Picture taken from ref. 4.
The crystalline phases of materials diffract x-rays according to the Bragg law is given by Eq. (2.11)\textsuperscript{20}

$$\lambda = 2d_{hkl} \sin \theta$$ \hspace{1cm} (2.11)

where $\lambda$ is the wavelength of the x-rays, $\theta$ is the angle between the atomic planes and the incident X-ray beam, and $d_{hkl}$ is the lattice spacing between (hkl) plane and for cubic crystals, it is given by Eq. (2.12)\textsuperscript{10}

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$ \hspace{1cm} (2.12)

where $a_0$ is the lattice constant of the crystal, as shown in Figure 2.10. The net scattering from all the atoms in a unit cell is a vector sum of the individual scattering vectors.\textsuperscript{20} This vector sum is known as the structure factor, $F_{hkl}$, given by Eq. (2.13)\textsuperscript{10}

$$F_{hkl} = \sum_i f_i(\theta) \exp[2\pi i (hx_i + ky_i + lz_i)]$$ \hspace{1cm} (2.13)

where $f_i(\theta)$ is the atomic scattering factor of $i$ atoms, $h$, $k$, $l$ are integers, $x_i$, $y_i$ and $z_i$ are coordinates of $i$ atoms. For the face centered cubic (FCC) structure associated with Ag, Pd, Cu and Ni, the coordinates of the atoms are\textsuperscript{10}

$$(x, y, z) = (0, 0, 0), \left(\frac{1}{2}, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \left(0, \frac{1}{2}, \frac{1}{2}\right)$$ \hspace{1cm} (2.14)

Therefore, the structure factor is given by Eq. (2.15)\textsuperscript{10}

$$F = f \{1 + \exp[\pi i (h + k) + \pi i (h + l) + \pi i (k + l)]\}$$

$$F = 4f \hspace{1cm} \text{if } h, k, l \text{ are all even or all odd}$$

$$F = 0 \hspace{1cm} \text{if } h, k, l \text{ are mixed even and odd}$$ \hspace{1cm} (2.15)
For example, the lowest-order diffractions from Cu, which has a FCC structure, are:
(111), (200), (220), (311), (222), (400), (331), (420).\textsuperscript{11}

If the crystal is 100 nm in size or smaller, particle peak broadening occurs. The
broadening can be utilized to estimate the sub-micron crystallite sizes in materials.\textsuperscript{20}
Assuming no residual strain induced broadening, the crystallite size broadening ($B$) of a
peak associated with the mean crystallite dimension ($\tau$) is given by the Scherrer
Eq. (2.16)\textsuperscript{21}
\[
\tau = \frac{K \lambda}{B \cos \theta_B}
\]
(2.16)
where $K$ is a shape factor and $B$ is the line broadening defined in Figure 2.11.

Figure 2.11. Broadening effect of fine crystallite size on a diffraction curve. A rough
measurement of $B$ is one-half the difference between two extreme angles at which the
intensity is zero. Alternatively, $B$ can be defined by the integrated intensity of the
diffraction peak. Picture taken from ref. 13.
Quantitative phase analysis is derived using the Rietveld method, originally conceived as a method of refining crystal structures using neutron powder diffraction data. The internal standard method is by far the most commonly used, given as Eq. (2.17)

\[
\frac{I_{(hkl)\alpha}}{I_{(hkl)\beta}} = k \frac{X_\alpha}{X_\beta}
\]

where \( X_\alpha \) is the initial weight fraction of phase \( \alpha \), \( X_\beta \) is the initial weight fraction of phase \( \beta \), the \( k \) value can be pre-established from standards of known concentration. Therefore, \( k \) permits the weight fraction of any unknown phase \( \alpha \) in the mixture to be calculated by the addition of a known amount, \( X_\beta \). The internal standard method is easily generated to the reference intensity ratio (RIR) method. The RIR method is the slope of the calibration curve for phase \( \alpha \) with internal standard \( \beta \) but has been normalized so that it may be calculated from any pair of diffraction lines in a calibration mixture.

2.6 Ultraviolet-Visible Spectroscopy (UV-Vis)

Absorption measurements based on ultraviolet and visible radiation in the visible region (from 200 to 400 nm) and adjacent ultraviolet region (from 400 to 800 nm) can be used to identify inorganic and organic species. The adsorption of ultraviolet and visible radiation usually is due to excitation of bonding electrons; therefore, the wavelengths of absorption peaks can be correlated with the types of bonds in the species. All organic compounds can absorb electromagnetic radiation because all contain valence electron that
can be excited to higher energy levels.\textsuperscript{25} The molecular orbitals associated with single bonds in organic molecules are known as sigma (\(\sigma\)) orbitals and the corresponding electrons are \(\sigma\) electrons. The double bond in an organic molecule contains two types of molecular orbitals: sigma (\(\sigma\)) orbital associated with one pair of the bonding electrons and a pi (\(\pi\)) molecule orbital responding to the other pair. The electrons corresponding with \(\pi\) orbitals are called \(\pi\) electrons. The charge-density distribution for antibonding sigma and pi orbitals are designated by \(\sigma^*\) and \(\pi^*\). Furthermore, many organic compounds contain nonbonding electrons designated as \(n\) electrons. The electronic transitions among certain energy levels can be brought about by the absorption of radiation. Four types of electronic transitions are possible: \(\sigma\rightarrow\sigma^*, \ n \rightarrow \sigma^*, \ n \rightarrow \pi^*, \ \pi \rightarrow \pi^*\).\textsuperscript{25} Transition metal ions can absorb visible light because their electrons in \(d\) orbital can be excited from one electronic state to another. The color of metal ion solutions is strongly affected by the presence of certain anions or ligands. UV-Vis spectroscopy is particularly effective for characterizing semiconductor nanoparticles or metal particles with a plasmon resonance in the 200-800 nm range. UV-Vis spectroscopy has also been used to reflect the change in particle size. As the particle size decreases in semi-conductor particles, the \(\lambda_{\text{max}}\) shifts to shorter wavelengths, due to the band gap increase of the smaller-sized particles.\textsuperscript{26} The optical spectra of semiconductors, for example MoS\(_2\), were sensitive to the size and shape of the clusters, the amount of aggregation, the surface structure, and the presence of any adsorbates.\textsuperscript{27} For metal nanoparticles, \(\lambda_{\text{max}}\) shifts to longer wavelength.
The UV-Vis spectrophotometer measures the intensity of light passing through a sample \((I)\) and compares it to the intensity of light before it passes through the sample \((I_o)\). The ratio \(I / I_o\) is the transmittance \((T)\). The absorbance \(A\) of the solution is given by Eq. (2.18), according to the Beer-Lambert law\(^{24}\)

\[
A = -\log (T) = -\log \left( \frac{I}{I_o} \right) = abc
\]  
\[(2.18)\]

where \(a\) is a constant known as the absorptivity, \(b\) is the path length through the sample, and \(c\) is the concentration of the absorbing species. The Beer-Lambert law indicates the absorptivity is a constant. The effect on the absorptivity of a given solute due to a change of solvent can not be predicted. The law provides no hint of the effect of temperature, the nature of the solvent, or the wavelength.\(^{28}\) There are three important causes of apparent deviation associated with the failure of the Beer-Lambert law.\(^{24}\) (1) The Beer-Lambert law is derived for monochromatic radiation, if the absorption band happens to be sharp or measurements are made at the steep slope of an absorption band, the absorption may well vary over the spectral bandwidth. (2) The existence of stray light may lead to noticeable bending of the analytical curves. (3) In Eq. (2.18), \(c\) represents the true concentration of the absorbing substance. With increasing concentration the experimentally observed absorbance may lag behind the theoretical absorbance resulting in curve is bent towards the concentration axis. Any interaction likely interferes with the electronic band structure in the absorbing species and energy absorption levels change with a resulting exhibition of a non-linear perturbation of Beer's Law.
Figure 2.12. Experimental configurations for (A) Thermal gravimetric analysis (TGA) and (B) Differential scanning calorimetry (DSC). TGA is performed on materials to determine changes in weight in relation to a change in temperature. DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and a reference material can be measured as a function of temperature. Pictures taken from ref. 29.
2.7 Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Thermochemical techniques are applied to determine thermodynamic changes in a batch of materials and reactions between the materials and the atmosphere. For thermogravimetric analysis (TGA), materials are suspended in a balance, and the weight is monitored during heating, cooling, or under isothermal conditions (Figure 2.12). Differential scanning calorimetry (DSC) measures the energy necessary to establish a nearly zero temperature difference between a substance and a reference material assumed to be thermally inert such as alpha-alumina, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. Differential scanning calorimetry can be used to measure a number of characteristic properties, such as oxidation, fusion and crystallization, as well as glass transition temperatures ($T_g$). In thermodynamics, endothermic describes a process or reaction that absorbs energy in the form of heat, for example melting of ice. Exothermic refers to a process or reaction that releases energy to the surroundings, such as oxidation. A basic principle underlies this technique: when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow into it than the reference material to maintain the same temperature in both. In the current work, DSC-TGA is measured by a simultaneous DSC-TGA (DSC-TGA 2960, TA Instruments Inc., New Castle, DE) with a temperature limit from ambient to 1500°C, and the balance sensitivity to 0.1 micrograms. In DSC mode, the noise is less than 4 microwatts.30
2.8 Zeta Potential Measurement

The common procedure for determining zeta potential is particle electrophoresis. Early work in this field has been reviewed by Overbeek\textsuperscript{31} and Booth\textsuperscript{32}. In electrophoresis, individual particles move under the influence of an applied electric field. Two general relationships are often used to describe the relationship between the electrophoretic mobility of a particle and the zeta potential (\(\zeta\)).

(I) The Helmholtz-Smoluchowski Eq. (2.19)\textsuperscript{33} applies for \(\kappa a > 100\):

\[
 u = \frac{\varepsilon \zeta}{\eta}
\]  

(2.19)

(II) The Hückel Eq. (2.20)\textsuperscript{33} applies for \(\kappa a < 0.1\),

\[
 u = \frac{2\varepsilon \zeta^3}{3\eta}
\]

(2.20)

where \(u\) is the particle velocity per unit potential field, \(\varepsilon\) is the dielectric constant of the liquid phase, \(\zeta\) is the average zeta potential, \(\eta\) is the liquid phase viscosity, \(\kappa\) is the Debye parameter (Eq. (1.6), \(\kappa^{-1}\) is referred to as the double layer thickness) and \(a\) is the particle radius. According to Eq. (2.19) and Eq.(2.20), the particle velocities are independent of size as long as the \(\kappa a\) restriction is met; they depend only upon zeta-potential \(\zeta\), the dielectric constant of the liquid phase \(\varepsilon\), and the liquid phase viscosity \(\eta\).

At 25°C, in ethanol the value of \(\kappa\) is 1.83\times10^8 m^{-1} with 10^{-3} M 1:1 electrolyte solution using Eq. (1.6). Calculated \(\kappa a\) values are listed in Table 2.1.
In 1931, Henry\textsuperscript{34} traced the discrepancy between Eq. (2.19) and (2.20). Smoluchowski assumed the electric field to be uniform and everywhere parallel to the particle surface. In contrast, Hückel ignored deformation of the applied field by the presence of the particle. Henry showed that when the external field is superimposed on the local field around the particle, the mobility is given by Eq. (2.21)

\[ u = \frac{2e\xi}{3\eta} \cdot f_1(\kappa a) \] (2.21)

The function \( f_1(\kappa a) \) depended on the particle shape and for a spherical particle, \( \kappa a < 1 \), \( f_1(\kappa a) \) is given by Eq. (2.22)\textsuperscript{35}

\[
f_1(\kappa a) = 1 + \frac{(\kappa a)^2}{16} - \frac{5(\kappa a)^3}{48} - \frac{(\kappa a)^4}{96} + \frac{(\kappa a)^5}{96} - \left[ \frac{(\kappa a)^4}{8} - \frac{(\kappa a)^6}{96} \right] e^\alpha \int_{\alpha}^\infty e^{-\tau} d\tau
\] (2.22)

For \( \kappa a > 1 \), \( f_1(\kappa a) \) is given by Eq. (2.23)\textsuperscript{35}

\[
f_1(\kappa a) = \frac{3}{2} \kappa a - \frac{9}{2\kappa a} + \frac{75}{2\kappa^2 a^2} - \frac{330}{\kappa^3 a^3}
\] (2.23)

It is noted that \( f_1(\kappa a) \) approaches 1 for small \( \kappa a \) and 1.5 for large \( \kappa a \)\textsuperscript{35}

De Keizer et al.\textsuperscript{36} calculated the electrophoresis mobility of randomly oriented charged cylinders. The average electrophoresis mobility of randomly oriented cylinder is obtained by taking a suitable average of the mobilities of a cylinder with its axis

<table>
<thead>
<tr>
<th>( a ) (nm)</th>
<th>( \kappa a )</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>1.83</td>
</tr>
<tr>
<td>20</td>
<td>3.66</td>
</tr>
<tr>
<td>30</td>
<td>5.49</td>
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perpendicular to the electric field and of one parallel to the field. It was derived when the relaxation effect is neglected; the electrophoretic mobility of a randomly oriented charged cylinder is obtained by adding one third of the mobility of a cylinder parallel to the field to two-thirds of its mobility perpendicular to the field.

Commercial instruments are available from Malvern Inc., Brookhaven Inc. and others to measure the zeta potential of a colloid suspension. The operation process is based on the principle of electrophoretic light scattering (or Doppler shift). An electric field is applied across a sample in solution, causing charged particles to migrate toward the opposite electrode. Light scattered from these particles will be Doppler or frequency shifted, and the magnitude of the Doppler shift depends on the particle zeta potential. The frequency shift (Δf) of the scattered light depends on the wavelength (λ) of the incident light, the particle velocity (u), and the light scattering angle (θ), as shown in Eq. (2.24)\(^{37}\)

\[
\Delta f = \frac{2u}{\lambda} \sin\left(\frac{\theta}{2}\right)
\]

In the current work, zeta potential has been measured using phase analysis light scattering (PALS, Brookhaven Instrument Corp., Holtsville, NY), which increases the performance associated with the conventional electrophoretic light scattering. The detection size limit of the PALS is from 5 nm to 30 μm with mobility ranging from 10\(^{-11}\) to 10\(^{-7}\) m\(^2\)/V.s.\(^{37}\) In addition, PALS can accurately measure samples that have low particle mobility, such as non-aqueous applications. Phase analysis light scattering (PALS) uses the same optical setup (Figure 2.13) as conventional electrophoretic light
scattering but with a different signal processing method. Measurement of the frequency shift of the colloid suspension is accomplished by heterodyning, wherein a fraction of the incident laser light is mixed with the frequency shifted scattered light. The mixing of the two frequencies results in the creation of a beat frequency (Figure 2.14). By definition, the phase is the product of the frequency and the time; therefore the frequency shift can be calculated from the phase shift. The phase shift is obtained at every point of the measured intensity for the heterodyned signal; the phase difference can be determined using a fraction of the beat wave.

Figure 2.13. Schematic of heterodyne optics used for zeta potential measurement. Picture is redrawn from ref. 37.
The complete electrophoretic mobility distributions in seconds can be measured using Zeta PLUS (Brookhaven Instrument Corp., Holtsville, NY). The frequency of the light scattered into the detector is shifted via the Doppler effect by an amount proportional to the velocity of the particles. A portion of the beam is split off and combined with the scattered beam after it is modulated at 250 Hz. In the absence of an electric field, a power spectrum of the signal from the detector would peak sharply at 250 Hz. With the application of an electric field, any resultant Doppler shift would occur at this frequency. If the resultant shift is less than 250 Hz, the zeta potential is negative, if greater than 250 Hz, the zeta potential is positive.

Figure 2.14. Schematic diagram illustrating an example in which the reference beam of a frequency $F_1$ is combined with scattered light arising from moving particles with frequency $F_2$. Combining the two frequencies produces a modulated beam due to constructive and destructive effects, which have a much smaller measurable frequency. This beat frequency is used to determine the mobility of the particles. Picture taken from ref. 38.
2.9 Surface Area by Gas Adsorption

The specific surface area (SSA) is defined as the surface area of the particles per unit mass or volume of material.\(^{29}\) Since the work of Brunauer, Emmett and Teller (BET),\(^{39}\) the surface area of a solid is of great importance in many chemical processes where gas or liquid reactions occur either on the surface or are influenced by the surface state. The basic assumption of the BET theory is that several layers of gas can be adsorbed on a solid surface. The amount of gas needed to form a monomolecular layer on the solid surface can be determined from the volume of gas adsorbed on the surface at different pressures at a constant temperature.\(^{40}\) In the current work, SSA is measured using a BET surface area analyzer (Gemini-2375, Micromeritics. Norcross, GA USA) with a measurement limitation from 1.0 m\(^2\)/g to 300 m\(^2\)/g.\(^{41}\) A schematic continuous-flow gas adsorption apparatus is illustrated in Figure 2.15.

![Schematic configuration of a continuous-flow gas adsorption apparatus.](image)

Figure 2.15. Schematic configuration of a continuous-flow gas adsorption apparatus. The amount of gas needed to form a monolayer on the solid surface can be determined by the volume of gas adsorbed on the surface at different pressures at a constant temperature. Nitrogen (N\(_2\)) is often used as the adsorbate gas and helium (He) is used as the carrier gas. The amounts of N\(_2\) adsorbed on the solid surface from a N\(_2\)-He mixture can be measured at the N\(_2\) liquefying temperature. Diagram taken from ref. 40.
With the isotherm of a gas adsorbed on a free surface, the BET theory results in the following Eq. (2.25)

\[ V = \frac{V_m c P}{(P_0 - P)(1 + (c - 1)P / P_0)} \]  

(2.25)

where \( V \) is the volume of the gas at 0ºC and 1 atmosphere pressure, \( P \) is the pressure, \( P_0 \) is the vapor pressure of the gas at the temperature of the adsorbent, \( c \) is a constant related to the heat of adsorption, and \( V_m \) is the volume of gas necessary to form a single layer over the entire surface. Putting Eq. (2.22) into a linear form results in Eq. (2.26)

\[ \frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{c - 1}{V_m c} \frac{P}{P_0} \]  

(2.26)

Plotting \( P/[V(P-P_0)] \) vs \( P/P_0 \), if Eq. (2.23) is valid, should give a straight line with slope \((s) = \frac{c - 1}{V_m c}\) and intercept \((I) = \frac{1}{V_m c}\). \( V_m \) and \( c \) are derived and expressed in Eq. (2.27)

\[ V_m = \frac{1}{s + I} \text{, and } c = \frac{s}{I} + 1 \]  

(2.27)

The specific surface area per unit mass \( S_M \) is given by Eq.(2.28)

\[ S_M = \frac{N_A V_m A_M}{V_{mol} M_S} \]  

(2.28)

where \( N_A \) is the Avogadro’s number, \( A_M \) is the area occupied by one adsorbate molecule \((16.2 \times 10^{-20} \text{ m}^2 \text{ for N}_2\)), \( M_S \) is the mass of the sample, and \( V_{mol} \) is the volume of 1 mole gas at the standard temperature and pressure of \( V_m \).
The major disadvantage of this method is that the sample is measured in a dry state. The precipitated materials may lose a substantial fraction of surface area on drying.\textsuperscript{43}

2.10 Related Computer Programs

\textbf{OPAL\textsubscript{1.9x} for Windows\textsuperscript{TM}.} \textsuperscript{44} OPAL is designed to be used for graphical display of metal hydrolysis systems, particularly solubility as a function of solution pH for metal oxide-hydroxide aqueous systems.\textsuperscript{44} OPAL has a database systems for many of the metal oxides-hydroxides of interest taken from that of Baes and Mesmer.\textsuperscript{45} Once the hydrolysis system has been defined, the various calculations necessary to produce the final plots were carried out by OPAL program. From the $\Delta G_f$ values, OPAL calculates expressions to represent the equilibrium reactions in plots of Log[concentration] as function of solution pH. OPAL produces four basic types of plots grouped two by two in terms of the ionic strength (I) of the system. For I = 0 two types of diagrams based directly on the free energy of formation can be displayed. Diagrams are drawn for ideal systems illustrating all possible reactions with no determination of stability fields and a resolved diagram showing stability fields or predominance areas. For I $\leq$ 0.3M a solubility diagram is plotted as well as a species distribution diagram. Calculation of species activity coefficients are based on Davies approximation to Debye-Hückel theory for activity coefficients with the Criss-Cobble method\textsuperscript{46, 47} used for high temperature extrapolation.
**STABIL4.5 for Windows™** The well-known theory of colloid stability was articulated by Derjaguin-Landau-Verwey-Overbeek (DLVO) in the 1940’s. DLVO theory deals with the potential energy resulting from superposition of the van der Waals attraction between particles and the repulsion potential energy due to electrostatic interaction between like-charged particle surface. The superposition of these two interactions gives the total interaction from which predictions can be made on the stability of a suspension. The computer program STABIL takes DLVO theory one step further by calculating interaction energy curves for systems where complex ionic equilibria are present and/or a polymer layer is present on the particles. (see Appendix 2 for detailed examples of STABIL 4.5)

**HSC Chemistry® for Windows 4.0.** The stabilities of ionic and no-ionic species in water solution are critical to investigating problems of corrosion, dissolution, leaching and selective precipitation. This information can be graphical illustrated by $E_h$-pH diagrams. The $E_h$-pH diagrams are produced by HSC Chemistry® in the current work. HSC Chemistry is a product of Outokumpu Research. However, the $E_h$-pH diagram calculation is based on the ideas from STABCAL-Stability calculations for aqueous systems-developed by Huang, at Montana Tech..

$E_h$-pH diagrams show the thermodynamic stability areas of different species in terms of suspension pH and on the electrochemical potential scale, with reference to standard hydrogen electrode (SHE). $E_h$-pH diagrams are useful to reveal at which pH and potential, metal is immune, dissolves or forms insoluble phases, such as oxides or hydroxides. It is noted that all dissolving species have the suffix “a” and the dotted lines in every $E_h$-pH diagram show the upper and lower stability limits of water. The diagrams
also take into account the concentrations of elements in aqueous phases and the pressure of the gas phase. However, kinetics of the reactions, that is, reaction rates and non-ideality of the mixtures, can not be predicted by the $E_h$-pH diagram.

2.11 References


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47. Criss, C. M.; Cobble, J. W., Thermodynamic properties of high temperature aqueous solutions .5. calculation of ionic heat capacities up to 200degrees . entropies + heat capacities above 200degrees. *Journal of the American Chemical Society* **1964**, *86*, (24), 5390-&.


Chapter 3

Synthesis of Nanoscale Silver Platelets: Dispersion and Determination of Thickness and Face Distribution

3.1 Introduction

Silver (Ag) nanoparticles have attracted increased attention due to their catalytic activity, excellent conductivity, chemical stability, anti-bacteriostatic effects, non-linear optical behavior and other applications. Several methods have been used to synthesize silver nanoparticles, including chemical reduction using NaBH$_4$, N$_2$H$_4$, ethanol, and N,N-dimethylformamide (DMF); epitaxial growth; photochemical reduction; chemical precipitation; Langmuir-Blodgett films and a self-assembly system.

To control the particle morphology, self-assembled molecular structures can be used as templates, wherein the synthesis is directed via a pre-existing structure upon which nucleation and growth take place. Andersson et al. synthesized silver nanospheres in polyoxyethylene (POE)-water system and polyoxyethylene (POE)/sodium bis(2-ethylhexy) sulfo succinate (AOT)-water system at room temperature using AgNO$_3$ water solution. The synthesized silver spheres had a diameter of 6 to 7 nm using POE-water system and had a diameter of 3 to 4 nm using the POE/AOT-water system, but no anisotropic particles were reported in this system. The octylamine / amylamine – water microemulsion system was utilized to make Ag platelets by Yener et al., who reported that the thickness of the aqueous layers increased with increasing R (R =
[water]/[surfactant]) ratio. Therefore, the thickness of the platelets could be controlled by adjusting the thickness of the aqueous layer.

The washing and dispersion of nanoparticles has become a barrier in various applications.\textsuperscript{16} Nanoparticles synthesized through self-assembly micro-emulsions require considerable steps to remove surfactant. Furthermore, maintaining the dispersion of the nanoparticles while laundering is critical. Approaches to dispersing nanoparticles have involved the formation of hydrophobic complexes at the particle/solution interface or the formation of a protective polymer layer.\textsuperscript{17, 18} Nanoparticle surfaces require protection to avoid the formation of a solid bridge at the contact region with other nanoparticles.\textsuperscript{19} For example, Rumpf and Schubert\textsuperscript{20} showed that agglomerates with solid bridges among particles are virtually impossible to separate. Wang et al.\textsuperscript{19} have recently shown in silica nano-composite colloids that the contact area is rapidly filled by solid material in nano-colloids. Thus, the protection-dispersion scheme consists of a transient, usually organic layer, to prevent the solid bridge formation and promote reversible flocculation during laundering to remove debris and detritus. Zsigmondy\textsuperscript{21} was the first to describe this protection in colloidal surface during dispersion. The notion of protection-dispersion, particularly for soluble components, has been described for several metal oxide systems including submicron (200 nm) (Mn, ZnFe)Fe\textsubscript{2}O\textsubscript{4}\textsuperscript{22}, 8 nm Y-doped ZrO\textsubscript{2}\textsuperscript{23} and 30 nm SiO\textsubscript{2} shell/Ag core nanocomposite colloids.\textsuperscript{24}

For this chapter, silver nanoplatelets were synthesized in the polyoxyethylene (POE)/water bilayer self-assembly system. The amine group in the octylamine used by Yener\textsuperscript{4} resulted in poor dispersion due to the strong binding at nanoplatelet surface prohibiting the ready removal of surfactant. As a nonionic surfactant, the hydrogen
bonding between the head group of POE and the Ag ions was expected to be less strong, making the removal of the surfactant after synthesis more efficient. Polyethylenimine (PEI) was used as the dispersant to obtain electrosteric stabilization of the silver nanoplatelet suspensions after synthesis. Based on the pH sensitive properties of PEI, a two-step protection-dispersion protocol was designed to efficiently launder and disperse Ag nanoplatelet colloids in an ethanol solution. At pH 9, a modest charge is associated with PEI, resulting in weakly flocculated nanoparticles. In the range of pH 6 to pH 7, the best combination of polymer conformation, a reasonable charge and modest ionic strength are obtained for good dispersion. The morphology of silver platelets was determined by atomic force spectroscopy (AFM), and transmission electron microscopy (TEM). AFM tip dilation along the face diameter direction was corrected by TEM analysis (n>100). Hydrodynamic diameter distributions were measured by quasi-elastic light scattering (QELS) based on the spherical particles methods in the commercial Malvern instrument. The zeta potential of the dispersed Ag nanoplatelet suspension was measured to evaluate the surface charge. For the first time, a protocol was developed to statistically evaluate the morphology of the tabular Ag nanoparticles using the AFM analysis for a relatively large population (n>200).

3.2 Materials and Methods

Silver nitrate (AgNO₃; ACS reagent, ≥ 99.0 wt%, Aldrich Chemical Co.) was used as the metal precursor. Polyoxyethylene (POE, C₁₂EO₄; Mn ~362, Aldrich Chemical Co.) was used as the surfactant to form the laminar bilayer phase with water
over a wide range of concentrations at 25 °C.\textsuperscript{25} Hydrazine hydrate (N\textsubscript{2}H\textsubscript{4}\cdot xH\textsubscript{2}O; reagent grade, Aldrich Chemical Co.) was used as the reducing agent. Polyethylenimine (PEI; Mw \textasciitilde 25,000, Aldrich Chemical Co.) was used as a polyelectrolyte to obtain electrosteric stabilization of silver nanoplatelets in colloidal suspension. Ethanol (200 Proof, J. T. Baker Chemicals) was used without further purification. Deionized water (specific conductivity less than 0.4 \times 10^{-7} \text{ S/m}) was used for all experiments.

In this study, nonionic polyoxyethylene (POE) was used as the amphiphile, and 0.04 M AgNO\textsubscript{3} aqueous solution was used to introduce Ag\textsuperscript{+} ions into the aqueous phase. Ag nanoplatelets were synthesized using a procedure modified from that of Yener et al.\textsuperscript{4,26} As shown in Figure 3.1, a 0.04 M AgNO\textsubscript{3} aqueous solution was slowly added to a defined amount of POE surfactant with a molar ratio R ([water]/[POE]) = 20. After the AgNO\textsubscript{3} addition (Eq. (3.1)), the mixture was stirred for 2 minutes at 120rpm to equilibrate the system. A white translucent precipitate was formed in the solution with the birefringence verified by polarized light microscopy. To prevent oxidative precipitation of the Ag\textsubscript{2}O, Ag\textsuperscript{+} was immediately reduced to Ag\textsuperscript{0} by the addition of hydrazine hydrate and an additional 2 minutes of stirring. Hydrazine hydrate was utilized as the reducing agent due to the advantage of reducing silver without additional heat, chemical treatment,\textsuperscript{27} or co-ion production (e.g. BO\textsubscript{3}\textsuperscript{2-}, B\textsuperscript{3-}, Cl\textsuperscript{-}, PO\textsubscript{3}\textsuperscript{-}, etc). With the reduction of hydrazine hydrate, Ag nanoparticle formation was identified by a color change from white translucent to dark grey. The system was equilibrated an additional 24 hours in darkness to ensure the complete reduction of the silver. The bilayer structure was decomposed by a pH-adjusted PEI-ethanol solution at a ratio of 1:5, and washed several times to remove the surfactant from the colloidal silver nanoplatelet suspension.
The pH of the PEI-ethanol solution was adjusted by a 0.2 M acetic acid ethanol solution for low PEI concentrations and a 2 M acetic acid ethanol solution for high PEI concentrations.

\[ 4 \text{Ag}^+ (\text{aq}) + \text{N}_2\text{H}_4(\text{aq}) + 4\text{OH}^- (\text{aq}) \rightleftharpoons 4\text{Ag}^0 (\text{s}) + \text{N}_2(\text{g}) + 4\text{H}_2\text{O} \quad E^\circ_{\text{cell}} = +1.96 \text{ V} \quad (3.1) \]

Figure 3.1. Flow diagram for the synthesis and dispersion of Ag nanoplatelets modified from Yener et al.\textsuperscript{4} Polyoxyethylene (POE) was used instead of the octylamine employed by Yener et al.\textsuperscript{4} \( R \) is the molar ratio of [water]/[surfactant]. The theoretical yield of the Ag nanoplatelets synthesis was 2.2 gram / liter with respect to total volume of the initial reaction system.
The synthesized Ag nanoplatelets were characterized by powder X-ray diffraction (XRD). The XRD patterns were recorded on a diffractometer (Pad V, Scintag, USA) operated at 35 kV and 30 mA with CuKα radiation. The size and morphologies of the Ag particulates were examined by atomic force microscopy (AFM, MultiMode IIIa, Digital Instruments, Santa Barbara, CA), and transmission electron microscopy (TEM, 2010LaB6, JEOL, Japan). The AFM samples were prepared by placing several drops of the ethanolic Ag nanoplatelet suspension on an atomically flat, freshly cleaved mica substrate and heating to 350°C to completely remove the organic layer. Preliminary experiments indicated no change in morphology with a heat treatment below ~ 400°C. TEM analysis was performed using lacy-carbon film on copper grids. Size distributions of both the face diameter and thickness were calculated on a number basis using offline AFM software (Nanoscope III version 5.12r3 Digital Instruments, Santa Barbara, CA) and image analysis software (Scion Image Beta 4.0.2., Scion Corporation, Frederick, MD). The hydrodynamic diameter distributions (HDDs) of the Ag nanoplatelet suspensions were determined on a Malvern Instrument based on quasi-elastic light scattering (Zetasizer Nano S, Malvern Instruments Ltd., UK). These hydrodynamic diameter distribution (HDD) results were deconvoluted based on a log normal distribution function using PeakFit® software (V4.12, Seasolve software Inc., USA). The zeta potentials of the Ag nanoplatelet suspensions were determined using a ZetaPALS analyzer based on the phase amplitude light scattering principle (Brookhaven Instruments Corp., Holtsville, NY).
3.3 Results and Discussion

3.3.1 Morphology of Silver Nanoplatelets

Theoretical Eh-pH-diagram shows the thermodynamic stability areas of different species in an aqueous solution. Figure 3.2 shows the Eh-pH diagram of Ag in an aqueous solution at 25°C. The stability areas of related species are presented as a function of pH and electrochemical potential scales. Three types of reactions among the species are represented in the diagram:28 (1) the horizontal lines represent the reactions involving only electron transfer, which are potential dependent; (2) the vertical lines represent the reactions involving only proton transfer, which are pH dependent; and (3) the sloped lines represent the reactions having both electron and proton transfer. Synthesis of Ag nanoplatelets was carried out at pH 10.4 in POE-water system with the use of 0.04 M AgNO₃ aqueous solution indicated by the solubility lines in the Eh-pH diagram of Ag-H₂O system. The $E^\circ_{cell}$ of the overall reaction equals to 1.96 V as indicated in Eq. (3.1) using hydrazine hydrate as the reducing agent.

The synthesized powder was a pure silver with cubic structure in an X-ray diffraction pattern similar to the previous study by Yener et al.4(not shown). No impurity peaks were observed, indicating the high purity of the final product. The TEM photomicrograph in Figure 3.3 shows the morphology of the Ag nanoplatelets obtained after the final wash in a 0.1 wt% PEI-ethanol solution at pH 6.5. The mean diameter of the Ag nanoplatelets is $37 \pm 4$ nm ($\pm 95\%$ confidence interval, $n = 5$). The Ag platelets were qualitatively thin judging by the transparency of the overlapped particles at the center of the image. The average thickness of the primary Ag platelets as determined by
AFM is $8 \pm 1\text{ nm}$ (± 95% confidence interval, $n = 5$) with an average face diameter of $40 \pm 2\text{ nm}$ (± 95% confidence interval, $n = 5$), as shown in Figure 3.4. The aspect ratio of the Ag platelets - the ratio of the platelet face diameter to its thickness is ~ 5.

Figure 3.2. $E_h$-pH-diagram of Ag-H$_2$O system at 25°C. The diagram is generated by HSC Chemistry®. Low $E_h$ values represent a reducing environment. High $E_h$ values represent an oxidizing environment. Dashed line (a) represents the potential of water saturated with dissolved O$_2$ at 1 atm (above this potential water is oxidized to O$_2$ and it is specified by the reaction: $2\text{H}_2\text{O} = \text{O}_2(\text{g}) + 4\text{H}(+a) + 4e^-$). Dashed line (b) represents the potential of water saturated with dissolved H$_2$ at 1 atm pressure (below this potential water is reduced to H$_2$ and it is specified by the reaction: $2\text{H}(+a)+ 2e^- = \text{H}_2\text{O}$). The lines with 00, -01, -02 and -03 represent the exponents for the molarities of Ag$^+$ ions in aqueous solution equilibrated with Ag, AgO$_2$ and Ag$_2$O species. The thermodynamic data used in plotting half cell hydrazine redox potential was generated by HSC Chemistry®.
Figure 3.3. Morphology of Ag nanoplatelets synthesized in POE-water bilayer system (R=20). The Ag nanoplatelets were washed in ethanol solution. The Ag nanoplatelet suspension was diluted in ethanol before being put on a lacy-carbon copper grid. Solid bridges at the contact region between particles indicated by arrows leads to irreversible aggregation during laundering of surfactant and spectator species.24
Figure 3.4. AFM image of Ag platelets synthesized with 0.04 M AgNO₃ as the Ag source, R = 20. The Ag nanoplatelets were synthesized in a POE-water bilayer system at room temperature and dispersed by 0.1 wt% PEI at pH 6.5. The AFM sample was prepared by placing drops of the Ag tabular particles on atomically flat and freshly cleaved mica substrate and then heating it to 350°C to remove the PEI layer. The removal of PEI is necessary to prevent PEI adhesion at the AFM tip. Tapping Mode™ was used for the AFM analysis.
3.3.2 Dispersion of Silver Nanoplatelets in Ethanol

The washing and dispersion of nanoparticles are crucial for the ultimate fabrication of structure using nanoplatelets. However, a persistent dilemma exists in these processes. If the nanoparticles are easily removed by sedimentation, the resulting agglomerates are difficult to re-disperse. In contrast, well-dispersed nano-particulates are difficult to separate from the solution phase, and a large number of nanoparticles can be lost in this manner after several washing iterations. In the current work, we used the pH dependent charging of polyethylenimine (PEI) to tailor the protection-dispersion approach. PEI is a hyper branched polymer that contains four different types of amine groups: primary, secondary, tertiary and quaternary as shown in Figure 3.5. In aqueous solutions, PEI is a pH-sensitive polyelectrolyte. At a high pH (pH ~ 10), PEI carries little positive charge due to the quaternary nitrogen. At lower pH ranges (pH ~ 6.5) the amine groups are highly protonated (~ 60% of the amines are charged). The degree of protonation of PEI amine group rarely exceeds 75%. To utilize the pH-dependent properties of PEI, a two-step protection-dispersion approach was developed to disperse the Ag nanoplatelets in an ethanol suspension. PEI was used to form a protective polymer layer with a low charge in initial washing iterations at pH 9, to promote reversible flocculation by polymer bridging while removing the surfactant. The pH solution was then adjusted to provide a positive charge in the final wash and promote electrosteric dispersion. However, PEI is also capable of self-aggregation by hydrogen bonding. Therefore, the self-aggregation behavior of the PEI molecules in ethanol was established prior to being applied in the protection-dispersion method for the silver nanoplatelets.
The hydrodynamic diameter distributions (HDD) of the PEI molecules were measured as a function of the PEI concentration in a range from pH 5.5 to pH 8.5 in ethanol. As shown in Figure 3.6 A-C, at pH 7.5 and pH 8.5, the PEI molecules tended to have a low charge from the quaternary amine groups. The secondary peaks might result from the hydrogen bonding among PEI molecules. At pH 6.5, the degree of protonation increased and the PEI molecules expanded. A unimodal HDD was obtained independent of the PEI concentrations (Figure 3.6D). No secondary or large peaks were attained in the HDD results at pH 6.5, indicating that the PEI had little or no self-aggregation in ethanol at ~ pH 6.5. At pH 6.5, the PEI molecules reached an intermediate state of protonation in which the number of donor sites and acceptor sites were balanced. At pH 5.5, the HDD was bimodal with large peaks over 1 micron size. This may be due to the

Figure 3.5. Branched chain structure of protonated polyethylenimine (PEI). PEI is highly branched, containing primary, secondary, tertiary and quaternary amine groups. PEI structure is modified from reference. Picture is drawn using ACD ChemSketch™.
higher ionic strength in the solution caused by the acetic acid introduced to the solution to reduce the solution pH. Figure 3.7 shows the conductivity of PEI in an ethanol solution as a function of pH and PEI concentration. The conductivity is proportional to the ionic strength. Therefore, a higher conductivity PEI-ethanol solution leads to a higher ionic strength in the solution. The hydrodynamic diameter results of PEI in ethanol were similar to those of PEI in a salt-free aqueous solution.
(B) 0.25 wt% PEI
- pH 5.5
- pH 6.5
- pH 7.5
- pH 8.5

Volume (%) vs. Diameter (nm)

(C) 0.5 wt% PEI
- pH 5.5
- pH 6.5
- pH 7.5
- pH 8.5

Volume (%) vs. Diameter (nm)
Figure 3.6. (A)-(C) Hydrodynamic diameter distributions of PEI in ethanol as a function of pH values. The suspension pH was adjusted by a 2 M acetic acid-ethanol solution. (D) Hydrodynamic diameter distribution of PEI in ethanol as a function of PEI concentrations at pH 6.5. A hydrodynamic diameter distribution measurement was performed based on quasi-elastic light scattering (QELS). From QELS diffusion, coefficients of the molecule are obtained, which can be transformed into hydrodynamic diameters using the Stokes equation.
Figure 3.7. The conductivity of salt-free PEI-ethanol solution as a function of suspension pH and PEI concentrations. 2 M acetic acid in ethanol solution was used to adjust the suspension pH. The conductivity is proportional to the ionic strength. Therefore, a higher conductivity PEI-ethanol solution has a higher ionic strength.
In a two-step protection-dispersion approach, initial washes were performed using a PEI at pH 9 to make the collection of nanoparticles more efficient. The surface of the Ag platelets was protected by the low charge PEI to prevent self-aggregation of the Ag nanoplatelets. The particles were well flocculated due to the small charge on the surface of the PEI. After three wash iterations to remove spectator ions and by-products of the chemical synthesis, the surfactant phase was removed, as no PEI peak observed by UV-Vis measurements of the supernatant. A final wash was conducted with PEI at pH 6.5, in which the highly charged PEI acted as an electrosteric dispersant to stabilize the Ag nanoparticles. Various PEI concentrations were used to disperse the Ag nanoplatelets in the final wash. As shown in Figure 3.8, within an optimum PEI concentration (~0.1wt %), the HDD of the Ag nanoplatelets had a narrow distribution with a high zeta potential and low ionic strength. Well-dispersed Ag nanoplatelets were obtained with the addition of 0.1 wt% PEI at pH 6.5 to the final wash without obvious agglomerations (Figure 3.4). At lower concentrations, the HDD had multiple modes due to low concentration of dispersant on the particle surfaces. At higher concentrations, ionic strength increased significantly. The increase in ionic strength resulted in compressed double layers around the particles and decreased the electrosteric repulsion afforded by the adsorbed, charged PEI molecules.
Figure 3.8. (A) Hydrodynamic diameter distributions of Ag nanoplatelets dispersed at various PEI concentrations at pH 6.5. (B) Zeta potential and conductivity of Ag nanoplatelets in ethanol as a function of PEI concentration at pH 6.5 (± 95% confidence interval, n = 5). The suspension pH was adjusted by a 0.2 M acetic acid-ethanol solution for low PEI concentrations and a 2 M acetic acid-ethanol solution for high PEI concentrations.
3.3.3 Statistical Study of Platelets Thickness and Face Distribution

Figure 3.9 shows the deconvolution of the most narrow hydrodynamic diameter distribution of Ag platelets at pH 6.5 using a log normal distribution function by area; the narrow distribution with a long tail yields three discrete peaks with central position ($\bar{d}$) and width parameter ($\sigma_z$) of: 16.1 nm, 0.161 (peak 1), 26.9 nm, 0.174 (peak 2) and 70.5 nm, 0.447 (peak 3) (Area ratio of the three peaks is: 3.2: 2.4:1. Goodness of fit $r^2 > 0.99.$). The three peaks may result from the tabular nature of the materials. Platelets with a narrow thickness direction perpendicular to the laser beam resulted in a mean particle size of 16.1 nm, while platelets with a face diameter perpendicular to the laser beam resulted in a mean particle size of 70.5 nm. The peak value of 26.9 nm originated from randomly orientated particles with respect to the laser beam; that is, the direction of thickness or face diameter exposed an angular range.

An inconsistency remained in the deconvolution of the HDD by quasi-elastic light scattering (QELS) (Figure 3.9) and the AFM particle morphology analysis (Figure 3.4). QELS technique relies on measuring the Brownian motion of small particles and relating this to the hydrodynamic diameter based on the assumption that particles are spheres.\textsuperscript{38} For non-spherical particles, the hydrodynamic diameter would be based upon the sphere which has the same average diffusion coefficient as that of the particles. In the well-dispersed Ag nanoplatelet suspension, Ag platelets were surrounded by PEI molecules. The hydrodynamic diameter measured by QELS included both the diameter of Ag platelet and (at least) the thickness of the PEI molecules on each face of the nanoplatelets.
Figure 3.9. Peak deconvolution of the hydrodynamic diameter distributions of the Ag platelet suspension dispersed in 0.1 wt% PEI at pH 6.5. The hydrodynamic diameter distribution was measured by quasi-elastic light scattering. A log-normal distribution function by area was used. The three discrete peaks with central position ($\bar{d}$) and width parameter ($\sigma_z$) are: 16.1 nm, 0.161 (peak 1); 26.9 nm, 0.174 (peak 2) and 70.5 nm, 0.447 (peak 3). The area ratio of the three peaks is: 3.2: 2.4:1. The goodness of fit $r^2 > 0.99$. 
The PEI has a layer thickness of ~ 1.4 nm, as determined via TEM holography by Yener et al.\textsuperscript{26} Therefore, for tabular particles, the QELS results lacked accuracy for the real particle morphology. In contrast, AFM analysis provides a high accuracy for determining the particle shape, and especially for determining the thickness of the particles due to a vertical resolution of less than 0.5 Å. However, the results lack statistical significance on account of the small particle population used in the development study by Yener et al.\textsuperscript{26}

To statistically evaluate the morphology of tabular particles, a protocol has been developed to statistically determine the shape of the platelets based on AFM analysis. According to the representative AFM images of the platelets, different color channels were set as a function of platelet thickness (i.e. each color channel represents a thickness range), as shown in Figure 3.10. A relatively large population of platelets (n>200) was examined and the number percent distribution of particulate thickness was determined by collecting the number of particles in each channel. Figure 3.11 shows the size distributions based on nanoplatelet thickness for 257 Ag nanoplatelets. The thickness of the Ag platelets has a bimodal distribution, with a mean thickness \( \bar{d} = \sum_{i=1}^{n} f_i d_i \)\textsuperscript{39} of 7 nm, and \( D_{50} = 7.1 \) nm from the cumulative distribution; both are consistent with the AFM results presented earlier in this study of 8 nm. Peak deconvolution using a log normal distribution function by area reflected three discrete peaks with central position \( \bar{d} \) and width parameter \( \sigma_z \): 3.2 nm, 0.402 (peak 1); 5.7 nm, 0.171 (peak 2) and 8.1 nm, 0.071 (peak 3). (The area ratio of the three peaks is: 1: 1.2 : 1.2. Goodness of fit is \( r^2 > 0.99 \).)
Figure 3.10. AFM image of Ag nanoplatelets synthesized in POE-water bilayer template using 0.04 M AgNO₃ as the Ag source (R = 20). Different color channels were set as a function of platelet thickness (i.e. Z height). The percent distribution of particulate thickness is determined by collecting the number of particles in each channel.
Figure 3.11. Cumulative and fractional distributions of thickness of Ag nanoplatelets (n = 257) synthesized in POE-water bilayer system. The fractional distribution was deconvoluted by a log-normal distribution function by area. The three discrete peaks with diameter (d) and width parameter (σ_z) are: 3.2 nm, 0.402 (peak 1); 5.7 nm, 0.171 (peak 2) and 8.1 nm, 0.071 (peak 3). The area ratio of the three peaks is: 1:1.2:1.2. The goodness of fit is r² > 0.99.
The face diameter of the Ag platelets was calculated using Scion Image™ analysis based on the AFM images. The procedure consisted of converting the AFM topography image into a black-and-white two-dimensional image, in which each platelet was black and the mica substrate was white in the background. The imaging software counted each area by assuming the isolated continuous black-colored area was an individual particle. Face diameter was calculated by assuming a circular shape. Figure 3.12 shows the size distributions of the face diameter for 257 Ag platelets. The mean face diameter \( \bar{d} = \sum_{i=1}^{n} f_i d_i \) was 38 nm, and \( D_{50} = 38 \text{ nm} \) according to the cumulative number percent distribution. Peak deconvolution showed three discrete peaks with central position \( \bar{d} \) and width parameter \( \sigma_d \): 28.5 nm, 0.198 (peak 1); 38.4 nm, 0.158 (peak 2) and 58.5 nm, 0.040 (peak 3). The area ratio of the three peaks is: 12: 31:1. The major particle size was \( \sim 38 \text{ nm} \) as shown by the major peak. The peak at \( \sim 58 \text{ nm} \) can be attributed to the presence of two primary particles in contact, particularly those with the 28.5 nm diameter. The platelet areas for the three peaks assuming a spherical shape are 638 nm², 1158 nm² and 2688 nm² for the 28.5 nm, 38.4 nm and 58.5 nm deconvoluted peaks, respectively. The corresponding ratios for the area are 1: 1.8: 4.2 for the 28.5 nm, 38.4 nm and 58.5 nm peaks. This suggests that the largest peak is a consequence of two 28.5 nm diameter particles touching. Given the greater relative number of the fine particles, this is a likely occurrence. This indicates that in order to get an accurate size distribution, the suspension must be well dispersed no matter which sizing technique is employed.
Considering the AFM tip dilation along the lateral direction, TEM analysis was performed on 100 Ag primary platelets to correct the measurements along the particle face diameter. The average face diameter of Ag nanoplatelets was $34 \pm 3$ nm, as obtained by TEM.

Figure 3.12. Cumulative and fractional distributions of face diameter of Ag nanoplatelets ($n=257$). The fractional distribution was deconvoluted by a log-normal distribution function by area. The three discrete peaks with diameter ($\tilde{d}$) and width parameter ($\sigma_z$) are: 28.5 nm, 0.198 (peak 1); 38.4 nm, 0.158 (peak 2) and 58.5 nm, 0.040 (peak 3). The area ratio of the three peaks is: 12: 31: 1. The goodness of fit is $r^2 > 0.99$.  

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3.4 Conclusions

Ag nanoplatelets have been synthesized with a self-assembly bilayer template using POE as the surfactant. Dispersion essentially starts by laundering freshly synthesized nanoparticles in most chemical synthesis methods so that the surfactant used in the synthesis may be removed from the solution phase. However, the washing and dispersion of nanoparticles tends to form aggregates due to the high surface relativities of the nanoparticles, and the strong van der Waals attraction between neighboring particles.\textsuperscript{40, 41} To minimize the effect of the attractive van der Waals among the particles, the suspension are stabilized using polymer additives evenly adsorbed on the particle surfaces. The resulting polymer layer masks the attraction, providing a repulsive force. If charged, electrosteric repulsion with a combination of electrostatic and steric effects leads to the repulsive energy. A protection-dispersion approach was established to stabilize the Ag nanoplatelets. The pH-dependent property of PEI in ethanol was established, which showed a similar trend to that of PEI in an aqueous environment. PEI was used as a polyelectrolyte with an optimum concentration of 0.1wt\% at pH 6.5. A statistical protocol has been developed to determine the morphology of tabular particles using an AFM analysis based on a relatively large population of platelets (n>200). Different color channels were set as a function of platelet thickness. By counting the number of particles of each color channel, the thickness distribution was determined. Face diameter distribution was obtained by transferring the AFM topography image to a black-and-white two-dimensional image, which was then analyzed. Comparing the TEM analysis to the AFM images of the same batch of as-synthesized Ag nanoplatelets, the
AFM tip effect could be neglected for platelets with an aspect ratio above 5. This protocol statistically evaluated the morphology of tabular shaped nanoparticles for the first time.

### 3.5 References


Chapter 4
High Yield Synthesis and Dispersion of Silver Nanoplatelets

4.1 Introduction

The synthesis and characterization of metal nanoparticles have gained considerable attention in past years due to their distinct properties compared to their bulk counterparts.\textsuperscript{1} Although a variety of methods have been reported for the preparation of nano-sized silver and silver composite platelets,\textsuperscript{2-7} most of the procedures yield stable silver dispersions only at relatively low concentrations, which are not suitable for large scale manufacturing. The synthesis of high yield nanoparticles with a controlled shape is persistent challenge. This topic has profound importance for both fundamental and applied research.

Using colloidal self-assembly as templates has been recognized as an effective means of controlling the particle morphology,\textsuperscript{8-13} wherein the growth and nucleation take place via a directed pre-existing structure. Most of the nanoparticles are nanometer size because of the nature of syntheses in the nano-reactors provided by self-assembled systems. A number of important metal systems have been synthesized using the colloidal self-assembly method, including Ag,\textsuperscript{14} Pd,\textsuperscript{15} Cu,\textsuperscript{16, 17} and Ni.\textsuperscript{18} Andersson et al.\textsuperscript{14} synthesized silver nanospheres in polyoxyethylene (POE)-water system and polyoxyethylene (POE)/sodium bis(2-ethylhexy) sulfosuccinate (AOT)-water system at room temperature using AgNO\textsubscript{3} water solution. The synthesized silver spheres had a
diameter of 6 to 7 nm using POE-water system and had a diameter of 3 to 4 nm using the
POE/AOT-water system, but no anisotropic particles were reported in this system. A
common approach to increasing the yield of the synthesis using self-assembly templates
is to increase the concentration of the salt precursor. The change in salt concentration
manipulates the formation of the desired colloidal template, and therefore affects the
synthesis parameters.

The effect of salt on the mutual solubility between water and organic compounds
was first studied by Lewith and Hofmeister. They determined the amount of
electrolyte necessary to salt out the globulin from a H2O-2 wt% globulin system. With
respect to the efficiency of sodium salts in salting out the globulin, the following order
has been established: 1/2Na2SO4 (1.60) > 1/2Na2CrO4 (2.6) > NaCl (3.63) > NaNO3
(5.42) > NaClO3 (5.52). The numbers represent the minimum amount of salt in
mole/liters to salt out the globulin. The smaller amount required for salting out, the more
efficient the electrolyte. For cations, Hofmeister found Li+ > K+ > Na+ > NH4+ > Mg2+
These series are called either as “Hofmeister” or as “Lyotropic” series. Neuberg reported that electrolytes with an inorganic and an organic ion increase the mutual
solubility between water and organic compounds. Such salts were considered part of a
“hydrotropic” series. Since the studies of Hofmeister and Neuberg, a number of
attempts have been devoted to quantifying the effect of the electrolytes. In the
thirties, Bruins ascribed a “lyotropic number” N to each ion, some of which are listed:
SO42- (N = 2) > Cl- (N = 10) > ClO3- (N = 10.7) > Br- (N = 11.3) > NO3- (N = 11.6)
A lower N leads to a more efficient corresponding anion.
Maintaining nanoparticulates as discrete units in colloids is essential in manipulating colloidal stability. A persistent dilemma in particulate synthesis and processing is the concentration required for high yield produce high ionic strength often leading to irreversible aggregation even when self-assembly systems are used for synthesis. Wang et al.\(^{30}\) have reported that solid bridges form at the neck of the SiO\(_2\) nanoparticles during the synthesis and washing using a reverse micelle approach resulting in irreversible aggregation. In order to stabilize the as-synthesized high yield Ag nanoplatelets while inhibiting aggregation, a protective action by organic species during the washing and concentration of the nanoparticles is required to prevent any liquid-mediated solid bridge formation. However, concentration of the organic dispersant should be minimized to achieve better functionalities for nanoparticles-based applications. Zsigmondy\(^{31}\) coined the term protection-dispersion for the notion that organic on nano colloids can be used to create protection barrier to prevent particle-particle contact and, hence, aggregation. Adair et al.\(^{32}\) have demonstrated that protection-dispersion can be used in several nanoparticulate material systems (e.g. ZrO\(_2\), \(\alpha\)-Al\(_2\)O\(_3\) and TiO\(_2\)) to produce stable nano colloids.

In the current work, silver nanoplatelets were synthesized using a polyoxyethylene (POE) – water self-assembly system in the lamellar phase region. A 1 M AgNO\(_3\) aqueous solution, used as the Ag source, increased the yield of Ag nanoplatelets to 20 g/l. The influence of the salt concentration (AgNO\(_3\)) on the presence of lamellar phase templates was monitored using polarized optical light microscopy. The morphology of the silver platelets was determined by atomic force spectroscopy (AFM) and transmission electron microscopy (TEM). The specific surface area of the high yield
Ag nanoplatelets was measured by BET. Polyethylenimine (PEI) was used as a polyelectrolyte to stabilize the colloid of the Ag nanoplatelets in ethanol. The adsorption isotherm of polyethylenimine (PEI) on the surface of the Ag nanoplatelets was determined by the amount of the dispersant adsorbed as a function of PEI equilibrium concentration. The surface charge of the Ag nanoplatelets in ethanol and PEI in ethanol were measured and the mechanism of interaction between the polyelectrolyte dispersant and the Ag metal platelets was discussed.

4.2 Materials and Methods

Silver nitrate (AgNO₃; ACS reagent, ≥ 99 wt%, Aldrich Chemical Co.) was used as the silver source. Polyoxyethylene (POE, C₁₂H₂₅(OCH₂CH₂)₄OH, Brij 30; Mn ~362, Aldrich Chemical Co.), hydrazine hydrate (N₂H₄· xH₂O; reagent grade, Aldrich Chemical Co.), polyethylenimine (PEI; Mw ~25,000, Aldrich Chemical Co.), and ethanol (200 Proof, J. T. Baker Chemicals) were used as received. Deionized water (with a specific conductivity of less than 0.4 × 10⁻⁷ S/m) was used for the synthesis.

4.2.1 Synthesis of Ag Nanoplatelets

Nonionic surfactant polyoxyethylene (C₁₂H₂₅(OCH₂CH₂)₄OH, POE) and aqueous molecules can self-assemble into a variety of thermodynamically stabilized microstructures, including micelles (L₁), and lamellar bilayers (Lₐ), which are physically not chemically associated (Figure 4.1 and Table 4.1).²² To synthesize tabular shaped
nanoparticles, self-assembly bilayers were used as template. The associated bilayer micro-reactors are soft and flexible due to van der Waals, hydrophobic, and hydrogen-bonding. The aqueous layers are able to act as domains for nucleation and growth of the particle synthesis.

Figure 4.1. Binary phase diagram of the POE (C\textsubscript{12}H\textsubscript{25}(OCH\textsubscript{2}CH\textsubscript{2})\textsubscript{4}OH) / water system. The \(L_1\), micellar solution, \(L_2\), surfactant liquid, \(L_\alpha\), lamellar phase, \(S\), solid and \(W\) phases are at equilibrium with a water containing surfactant monomer. The marked area indicates the range of the study on the presence of the bilayer phase (\(L_\alpha\)) as a function of AgNO\textsubscript{3} concentrations. High yield synthesis (20 g/liter) of the Ag nanoplatelets was carried out at \(R = 5\). Diagram modified from ref. 22. Regions A, B, and C areas are referred in Table 4.1.
Table 4.1. Lamellar bilayer phase ($L_\alpha$) formation map as a function of AgNO3 concentrations at 25°C (corresponding to the marked area in Figure 4.1). A, B and C represent the following regions observed under polarized light microscope: (A) region has no lamellar phase, (B) region has a pure lamella bilayer ($L_\alpha$) and the Maltese crosses can be visualized which fill the field of view, (C) region has a water and lamellar bilayer mixture ($W + L_\alpha$). The birefringence can be visualized in a local area. Region A, B, and C correspond to areas in Figure 4.1.

<table>
<thead>
<tr>
<th>AgNO3 Conc.</th>
<th>R</th>
<th>57.3 POE 26wt%</th>
<th>46.9 POE 30wt%</th>
<th>20.1 POE 50wt%</th>
<th>16.5 POE 55wt%</th>
<th>13.4 POE 60wt%</th>
<th>8.6 POE 70wt%</th>
<th>5.0 POE 80wt%</th>
<th>4.1 POE 83wt%</th>
<th>3.3 POE 86wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04 M</td>
<td>A</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>C</td>
<td>A</td>
</tr>
<tr>
<td>0.3 M</td>
<td>A</td>
<td>C</td>
<td>C</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>0.5 M</td>
<td>A</td>
<td>A</td>
<td>C</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>0.75 M</td>
<td>A</td>
<td>A</td>
<td>C</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>1.0 M</td>
<td>A</td>
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<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>C</td>
</tr>
</tbody>
</table>

(A) Bilayer

(B) Air Bubbles

(C) Air Bubbles
With the formation of a bilayer phase, birefringence is observed under polarized optical microscopy. Birefringence (or double refraction) is an optical property of anisotropic crystals and structures such as bilayers. Anisotropic crystal structures transform an incident light beam into two perpendicular polarized rays, the ordinary (o) ray and the extraordinary (e) ray, which propagate at different velocities in the medium. Due to the different propagation velocities, the waves of the two rays are out of phase by optical retardation $\delta$, and the medium exhibits different refractive indices, $n_e$ (extraordinary) and $n_o$ (ordinary), with respect to the two rays. The difference is a measure of the degree of birefringence, Eq. (4.1)\(^\text{34}\)

$$\Delta n = n_e - n_o$$  \hspace{1cm} (4.1)

$\Delta n$ is related to the retardation by Eq. (4.2)

$$\delta = 2 \pi l \frac{\Delta n}{\lambda}$$  \hspace{1cm} (4.2)

where $l$ is the path length of the sample and $\lambda$ is the wavelength of the incident light in a vacuum. In the current work, a map of the bilayer phase as a function of AgNO$_3$ concentration and R value ($R = \text{molar ratio of [water] /[POE]}$) was obtained at 25ºC. A thermal bath was used to control the temperature fluctuation to within ± 0.2ºC.

High yield (20 g/l) Ag nanoplatelets were prepared via the procedure described in chapter 3 (Figure 3.1). A 1 M AgNO$_3$ aqueous solution was added to POE in a molar ratio of 1:5, then stirred at ~ 120 rpm for two minutes. A lamellar phase formed which was birefringent under polarized light microscopy. The Ag$^+$ was immediately reduced to Ag$^\circ$ by the addition of hydrazine hydrate (N$_2$H$_4$·xH$_2$O) and another two minutes of stirring. The color change of the precipitate from white to dark gray indicated the silver
reduction. The system was allowed to equilibrate for another 24 hours without light to ensure complete reduction. After this equilibration, ethanol was used to decompose the bilayer phase in a volume ratio of 10:1. The washing of the Ag nanoplatelets was carried out with centrifugation. The Ag nanoplatelets were first centrifuged at 3000 rpm for 5 minutes. The solid particles were collected and redispersed in ethanol. This washing procedure was repeated three times to remove the surfactant (POE). The residual concentration of POE was monitored by UV-Vis spectra.

4.2.2 Characterization of Ag Nanoplatelets

After the final wash, the Ag tabular nanoparticles were dried in air at room temperature for phase identification. Phase identification was performed using an X-ray diffractometer (XRD, Pad V, Scintag, USA) operated at 35 kV and 30 mA with CuKα radiation. The morphologies of the Ag particulates were observed with an atomic force microscope (AFM, MultiMode, Digital Instruments) using Tapping Mode™. The AFM samples were prepared by placing drops of the Ag tabular particles on a molecularly cleaved, pristine mica substrate. Transmission electron microscopy (TEM, 2010LaB6, JEOL, Japan) was performed at an accelerating voltage of 200 kV. A droplet of the Ag nanoplatelet suspension was put on a holey carbon copper grid and dried at room temperature. The specific surface area (SSA) was measured using the BET method with N₂ as the absorbate gas (Micromeritic Gemini 2375). The SSA of the Ag nanoplatelets was measured at 50°C after they were held for 2ⁿ (n = -1, 0, 1, 2, 3, 4, 5) hours in a vacuum.
4.2.3 Polyethylenimine Adsorption Isotherms

Polyethylenimine (PEI) was used as a polyelectrolyte to disperse the Ag nanoplatelets in ethanol solutions. The adsorption of polyethylenimine (PEI) on the surface of the Ag nanoplatelets was measured by the amount of the adsorption density as a function of PEI equilibrium concentrations at room temperature. By equilibrating a known amount of Ag nanoparticles, an adsorption isotherm was created by increasing the amount of the PEI dispersant until a constant adsorption plateau was obtained.

Figure 4.2. UV-Vis spectra showing the absorption peaks of polyoxyethylene (POE) in ethanol, and polyethylenimine (PEI) in ethanol due to the unsaturated bonds that existed in the chemical structure. Ethanol absorbs very weakly above 200 nm, which makes it a good solvent medium.\textsuperscript{35}
UV-Vis spectra were used to detect the difference in PEI concentration before and after adsorption. In order to quantitatively assess the amount of dispersant adsorbed, UV-Vis spectroscopy reference curves were constructed for ethanol, POE in ethanol and PEI in ethanol, as shown in Figure 4.2. The adsorption isotherm procedure was illustrated in Figure 4.3. The initial PEI concentration ($C_0$) in solution was determined by UV-Vis spectroscopy prior to the adsorption. Suspensions containing 2 wt% Ag nanoplatelets were prepared in ethanol that contained various concentrations of PEI from pH 6 to pH 9. The solution pH was adjusted by a 2 M acetic acid ethanol solution and a 0.1 M tetramethyl ammonium hydroxide (TMAOH) ethanol solution. All of the suspensions were shaken overnight on a shaker (Eberbach Corporation, Ann Arbor, Michigan, USA) to obtain equilibrium followed by centrifugation at 12,000 rpm for 2 minutes. Preliminary experiments were performed on PEI-ethanol solutions shaking overnight and verified that the vibration force had no change in PEI concentrations prior to and after shaking. After centrifugation, the equilibrium concentration ($C_e$) of PEI in the supernatant was measured by UV-Vis spectroscopy measurements based on the Beer-Lambert law. The adsorption density ($\Gamma$) was calculated thereafter with Eq. (4.3) according to the difference between initial concentration and after adsorption,

$$\Gamma = \frac{C_{adv}M_S}{M_{Ag} \cdot SSA_{Ag}} \quad (4.3)$$

where $M_S$ is the mass of PEI solution, $M_{Ag}$ is the mass of Ag nanoplatelets in suspension, and $SSA_{Ag}$ is the specific surface area of Ag nanoplatelets. PEI concentration used in this study was based on weight percent. The zeta potentials of PEI in ethanol and Ag platelets in ethanol as a function of pH were determined by particle electrophoresis with a
phase analysis light scattering (PALS) system (ZetaPALS, Brookhaven Instruments Corp., Brookhaven, NY). Ag nanoplatelets concentration was maintained at 0.01 vol% for zeta potential determination. All of the determinations were performed at 25°C. All the pH measurements were carried out with a Sentron ISFET pH probe (Argus IP 65 ISFET probe, Sentron Inc., WA) and calibrated against standard aqueous buffer solutions.

![Figure 4.3. Schematic illustration of PEI adsorption on the surface of Ag nanoplatelets. (A) PEI in ethanol with an initial concentration of $C_0$; (B) With the addition of Ag nanoplatelets, PEI is adsorbed on the particle surface; (C) After centrifugation, PEI adsorbed on the surface of the platelets settles out of the solution with dense Ag. The concentration of excess PEI ($C_e$) can be determined from the concentration in the supernatant. Therefore, the absorbed PEI concentration can be calculated using $C_{abs} = C_0 - C_e$. The PEI concentrations were measured by a UV-Visible spectrum using the Beer-Lambert law.](image-url)
4.3 Results and Discussion

4.3.1 Salt Effects on the Water-Polyoxyethylene Bilayer System

In the POE-water phase diagram (Figure 4.1), without the addition of AgNO₃, the bilayer phase ($L_\alpha$) formed with a wide range of POE compositions from 26 wt% to 86 wt%. With an increase in Ag⁺ (aq) concentrations, the presence area of pure lamellar phase (region B) decreases. A bilayer formation map as a function of AgNO₃ concentrations and R values was obtained by observing the occurrence of the birefringence under polarized optical light microscopy (Table 4.1). Correspondingly, region A has no micelle solution ($L_2$) or lamellar phase ($L_\alpha$), region B has only a pure bilayer phase ($L_\alpha$), and the Maltese crosses can be visualized by polarized light microscopy, and region C represents water ($W$) and bilayer ($L_\alpha$) mixed phases. A pure bilayer phase regime was required as a template for the synthesis of tabular-shaped particle. With 0.04 M AgNO₃, a lamellar phase was present from 30 wt% POE to 80 wt% POE. Increasing the AgNO₃ concentration from 0.3 M to 1 M gave pure lamellar phases in a more narrow range from 55 wt% POE to 83 wt% POE, which corresponds to R values of 16.5 and 4.1, respectively. It is known that cations are smaller and have more water of hydration than anions. Therefore the phase boundary shift was not primarily caused by the competition between the ions for free water, but by specific anion and cation effects. It is likely that the increased salt concentration affected the interaction between the molecules, to decrease the presence of the bilayer phase boundary with a shift toward the surfactant-rich end. With the increase of $[\text{NO}_3^-]$ concentration,
oxyethylene-water interaction decreased due to dehydration of the POE head group as discussed earlier, where phase separation was induced when the ion concentration reached the upper limit. Consequently, the [water]/[surfactant] molar ratio decreased to compensate for the dehydration of the POE head groups and therefore to maintain the bilayer phase structure.

4.3.2 Morphology of Ag Nanoplatelets

The phase identification through X-ray diffraction showed that the as-synthesized powders were pure silver without any impurities (Figure 4.4). The size and shape of the platelets generated from the bilayer system depended on the molar ratio of water to surfactant, R. The general trend for the growth of Ag platelets is that silver thickness is proportional to R. TEM photomicroscopy (Figure 4.5) shows that the mean diameter of the obtained Ag nanoplatelets is 58 ± 4 nm. Without the PEI protection-dispersion, Ag nanoparticles formed solid bridges in the ethanol solution. The AFM analysis of Ag nanoplatelets with PEI protection-dispersion shows that the primary particles of the high yield Ag platelets have an average thickness of 8 ± 1 nm and an average face diameter of 59 ± 3 nm (± 95% confidence interval, n = 5), as shown in Figure 4.6. A statistical evaluation of the morphology of the Ag nanoparticles was conducted using the AFM protocol described in chapter 3. Figure 4.7 shows both the cumulative and fractional number percent distributions of the thickness of 277 Ag nanoplatelets derived from the same synthesis approach. The thickness of the Ag platelets has a bimodal distribution,
with a mean thickness \( \bar{d} = \left( \sum_{i=1}^{n} f_i d_i \right)^{37} \) of 7 nm, and a \( D_{50} = 6.3 \) nm from the cumulative distribution. The face diameter of the high yield Ag platelets has a tri-modal distribution, with peak values of 30.6 nm, 63.5 nm and 103.6 nm. The large peak values were mainly due to the agglomeration tendency among particles. The arithmetic mean face diameter \( \left( \bar{d} = \sum_{i=1}^{n} f_i d_i \right)^{37} \) is 55 nm, with the median value (i.e., at 50% of the population) of 53 nm from the cumulative distribution. The platelet areas for the three peaks assuming a spherical shape are 735 nm\(^2\), 3167 nm\(^2\) and 8430 nm\(^2\) for the 30.6 nm, 63.5 nm and 103.6 nm deconvoluted peaks, respectively. The corresponding ratios for the area are 1: 4.3: 11 for the 30.6 nm, 63.5 nm and 103.6 nm peaks. This suggests that the largest peak is a consequence of two or three 30.6 nm diameter particles touching. Given the greater relative number of the fine particles, this is a likely occurrence. Compared to the synthesis results discussed in chapter 3, the tabular Ag nanoparticles had thicknesses in the same range as the low yield Ag nanoplatelets. However, the face diameter was 1.5 times larger than that of the low yield platelets. In the growth procedure, particles grew both parallel and perpendicular to the phase boundaries. It is likely that the higher concentration (25 times higher) of Ag\(^+\) ions leads to more rapid diffusion of ionic species parallel to the phase boundaries where little constraint occurs, and produces higher aspect ratio platelet particles.
Figure 4.4. X-ray diffraction pattern of Ag nanoplatelets prepared in a polyoxyethylene (POE)-water bilayer system and reduced by hydrazine hydrate at room temperature. The tabular Ag nanoparticles were washed three times in ethanol. XRD verified that the synthesized phase pure Ag nanoplatelets do not have a specific crystallographic orientation.
Figure 4.5. TEM morphology of Ag nanoparticles synthesized in a POE-water bilayer system without the protection of PEI. Without protection-dispersion, solid bridges at the contact region between particles, with an example indicated by the arrow, lead to irreversible aggregation during laundering of the surfactant and other spectator species.30, 32, 38
Figure 4.6. AFM images of Ag nanoparticles prepared in a POE-water bilayer system. Tapping Mode™ was used for the AFM analysis. The sample was prepared by placing drops of the ethanolic Ag nanoplatelet suspension on atomically flat, freshly cleaved mica. The Ag nanoplatelets had an average thickness of $8 \pm 1$ nm and an average face diameter of $59 \pm 3$ nm ($\pm 95\%$ confidence interval, $n = 5$).
Figure 4.7. (A) Cumulative and fractional distributions (number%) of thicknesses of high yield Ag platelets. The fractional distribution was deconvoluted by a log-normal distribution function by area. The four discrete peaks with diameter \( \bar{d} \) and width parameter \( \sigma_z \) are: 2.5 nm, 0.639 (peak 1); 5.9 nm, 0.220 (peak 2) and 10.6 nm, 0.096 (peak 3) and 13.6 nm, 0.123 (peak 4). The area percent of the four peaks is: 26%: 52%: 9%: 13%. The goodness of fit is \( r^2 > 0.99 \). (B) Cumulative and fractional distributions (number %) of face diameters of high yield Ag nanoplatelets. The fractional distribution was deconvoluted by a log-normal distribution function by area. The three discrete peaks with diameter \( \bar{d} \) and width parameter \( \sigma_z \) are: 30.6 nm, 0.285 (peak 1); 63.5 nm, 0.279 (peak 2) and 103.6 nm, 0.079 (peak 3). The area percent of the four peaks is: 22%: 66%: 12%. The goodness of fit is \( r^2 > 0.99 \). Based on 277 particles synthesized using 1 M AgNO\(_3\) as the Ag source (R = 5).
4.3.3 Specific Surface Area

Specific surface area (SSA) is sensitive to variations in the shape and size of particles finer than about 1 μm. The Ag nanoparticles were heated to 50°C and maintained for various times, then cooled to 25°C for the SSA measurement. The SSAs of the Ag tabular particles as a function of heating time were measured under a vacuum (30m Torr) using the N₂-adsorption BET method. At 50°C, the SSA increased slightly from 0.5 hours of treatment to the 4 hour mark and then decreased from the 4 hour mark to the 8 hour mark, before achieving a plateau in SSA (Figure 4.8). The maximum SSA was ~17.5 m²/g when the Ag platelets had been heated for 4 hours.

The theoretical specific surface area of the Ag nanoplatelets was calculated based on two assumptions: (1) nanoplatelets are well dispersed without agglomeration, and (2) particles are uniform, without significant dimensional variation in face diameter or thickness. The specific surface area of an individual particle is calculated based on the tabular shape, as given by Eq. (4.4)

\[
SSA = \frac{2A_1 + A_2}{A_1 \cdot t \cdot \rho} \text{ (m}^2/\text{g)}
\]  

(4.4)

where \(\rho\) is the density of the Ag platelets, \(A_1\), \(A_2\), and \(t\) are defined in Figure 4.9.
Figure 4.8. Specific surface area as a function of heating time for high yield Ag nanoplatelets prepared in a POE-water bilayer system. The Ag nanoplatelets had an average thickness of $8 \pm 1$ nm and an average face diameter of $59 \pm 3$ nm ($\pm 95\%$ confidence interval, $n = 5$). The Ag nanoplatelets were heated at 50ºC in a vacuum and maintained for various time periods.

Figure 4.9. Geometry of a platelet particle, in which $d$ is the face diameter and $t$ is the thickness of the particle. $A_1$ is the area on upper side, which is the same as the bottom side and $A_2$ is the area of the periphery.
The difference of SSA between the theoretical calculation and the BET measurement mainly resulted from the assumptions about the model and actual state of the Ag platelet system. From the theoretical prediction, the SSAs of Ag nanoplatelets as a function of face diameter and thickness are plotted in Figure 4.10. At a given thickness, SSA initially decreases steeply with increase in face diameter and reaches a plateau. With a fixed average face diameter, SSA decreases with the increase in average platelet thickness. The predicted SSA of Ag nanoplatelets with an average thickness of 7 nm and an average face diameter of 60 nm is ~ 30 m²/g, and decreases to ~ 19 m²/g when the thickness increases to 15 nm, as shown in Figure 4.10A. At a given face diameter, SSA initially decreases steeply with increase in thickness and reaches a plateau. With a fixed average thickness, SSA decreases with the increase in average face diameter. The SSA is more sensitive to the variation of thickness than that of face diameter. The remaining surfactant on the particle surface, the degree of aggregation of the nanoplatelets after drying and the platelets with large average face diameter (~ 100 nm) and thickness (~15 nm) are all factors that lead to a lower measured specific surface area than theoretically calculated.
Figure 4.10. (A) The theoretical specific surface area of Ag nanoplatelets as a function of the face diameter; (B) The theoretical specific surface area of Ag nanoplatelets as a function of platelet thickness according to Eq. (4.4), in which $t$ is the average thickness of Ag nanoparticles. The SSA is more sensitive to the variation of thickness than that of face diameter.
4.3.4 Adsorption of Polyethylenimine on Ag Nanoplatelets

Polyelectrolyte adsorption on inorganic surfaces is attributed to the following factors: (1) the surface area and the surface charge of the adsorbent; (2) the degree of dissociation of the polyelectrolyte; (3) the amount of polymer present; (4) the interaction of the polyelectrolyte and the adsorbent; and (5) the properties of the solution (e.g., ionic strength). Adsorption from the solution at the solid-liquid interface is surface-dependent and provides valuable information for characterizing the nature of the particle surface. Polyelectrolyte adsorption is also essential in electrosteric dispersion of colloidal suspensions. The driving force for adsorption of a dispersant is associated with a decrease in free surface energy. However, the interactions at interfaces are complex, especially when polymeric dispersants are used. The amount of dispersant is governed by the particle-dispersant attraction and the attraction or repulsion among the adjacent dispersant molecules adsorbed on the particle surface. Attraction between extended polymer chains of an adsorbed polymeric dispersant contribute to a favorable free energy change and enhance adsorption in multilayers, while repulsion leads to saturated monolayers.

Polyethylenimine (PEI) has been commonly used as a polyelectrolyte to improve the stability of ceramic suspensions. The titration curve of a 1 wt% PEI in aqueous solution by HNO₃ is presented in Figure 4.11. The neutralization reaction of PEI was distinguished by a proton transfer process from the solution to the polymer skeleton. For values greater than pH 11, PEI has a low degree of proton association and carries little or no charge. At this highly alkaline pH regime, the degree of adsorption is
relatively insensitive to ionic strength or charge density on the adsorbent. At lower pH values, PEI has a higher degree of proton association and carries positive charge. The amount of adsorption is dependent on both ionic strength and adsorbent charge density. The PEI used in the current work was highly branched with this pH-dependent charging properties. When PEI is applied to a negatively charge particle surface, the adsorbed cationic PEI molecules adsorb in a flat configuration via the electrostatic interactions between the PEI molecules and the oppositely charged adsorbate surface. Based on prior AFM studies, PEI adsorbs on silver nanoplatelets with an adsorption thickness of ~1.4nm.

Figure 4.11. Protonation of the amine groups as a function of pH in water at 298 K.
The electrophoretic mobility of the Ag nanoplatelets was measured in ethanol over the pH range from pH 3 to pH 9. The isoelectric point of the as-synthesized Ag nanoplatelets in ethanol was ~ pH 5, as shown in Figure 4.12. The Ag nanoplatelets became negatively charged when pH >> pH 5, whereas from pH 6.5 to pH 9, the PEI was positively charged in ethanol and the surface charges decreased in the alkaline region. At neutral pH, the hydroxyl groups on the Ag surface provided the surface-active sites for the highly protonated PEI molecules. The adsorption mechanism of the PEI on the Ag nanoparticles was dominated by electrostatic interactions, where the Ag nanoplatelets and PEI molecules were oppositely charged. At higher degrees of dissociation, the electrostatic forces promoted adsorption until the surface charge became neutralized.

The isotherm shapes are largely determined by the adsorption mechanism and can be used to reveal the nature of the adsorption. The adsorption density (Γ) of PEI on the Ag nanoplatelets as a function of PEI equilibrium concentration are plotted in Figure 4.13. It is shown that six adsorption isotherms obtained as a function of solution pH are of the Sigmoidal isotherm (S-isotherm) with various saturation adsorption values. The characteristic feature of the obtained S-isotherm curves shows low adsorbability at low PEI equilibrium concentrations, followed by a rapidly increased adsorbability. The rapidly ascending part of the isotherm is similar to the normal Langmuir isotherm. This characteristic feature indicates cooperative adsorption for the PEI molecules on the Ag nanoplatelets. Cooperative effects rise due to molecular binding to a surface better when the molecule interacts with a neighboring adsorbed molecule. In other words, an adsorbed molecule is more stable when it is adjacent to other already adsorbed molecules.
Figure 4.12. Zeta potential of Ag nanoplatelets and PEI as a function of pH in ethanol solutions. The solid loading of the Ag nanoplatelet suspension was 0.01 vol%. The suspension pH was adjusted by an acetic acid solution in ethanol. The pH of the suspensions was measured with an ISFET pH meter calibrated against standard aqueous buffer solutions. The error bars are ± 95% confidence interval, n = 5.
Figure 4.13. Adsorption isotherm of PEI on Ag nanoplatelets as a function of equilibrium PEI concentration at various pH values. The maximum adsorption density occurs at suspension pH 7 and is associated with the electrostatic force between the negatively charged Ag surface and the positively charged PEI. The lines are fitted by Sigmoidal function. Parameter values obtained from the fitting of the experimental data are listed in Appendix A. Curve fitting of adsorption data via Origin® 6.0 for the S-shaped adsorption isotherm.
In practice, the S-isotherm usually appears when three conditions are satisfied:\textsuperscript{50} the adsorbent molecule (1) is monofunctional, which means the molecule has a marked localization of attractive force for the adsorbate over a short section of its periphery, and that it is adsorbed as a single unit; (2) has moderate intermolecular attraction, causing it to pack towards vertically in regular array in the adsorbed layer; and (3) meets strong competition, for adsorbate sites, from molecules of the solvent or of another adsorbed species. These conditions were fulfilled in the current adsorption study of PEI polyelectrolyte molecules on the surface of Ag nanoplatelets in ethanol solution. Polyelectrolytes cause flocculation via electrostatic attraction, such as the charge-patch model and bridging mechanisms. In the S-isotherm, the initial slope near the discontinuity indicates that at low PEI equilibrium concentrations, the isolated PEI molecules lie flat on the Ag surface. As the molecules approach each other with increasing concentration, lateral interactions come into play among the highly branched PEI molecules, and ultimately cause the flat molecules to be pulled toward each other.\textsuperscript{51} The PEI molecule is more stable in the adsorbed state when it is adjacent to other already adsorbed PEI molecules due to cooperative effect.\textsuperscript{50} The PEI self-aggregation effect in the previous study (details see Chapter 3) supported this cooperative effect. Also, as shown in Figure 4.13, the reflection points of the S-isotherms for the six curves appear to be near the 0.1 wt\% PEI equilibrium concentration. This indicates that PEI has a great tendency to adsorb in a flat configuration at equilibrium concentration below \( \sim 0.1 \) wt\%. The previous study (in Chapter 3) verified that \( \sim 0.1 \) wt\% PEI was the optimum PEI concentration for dispersion of Ag nanoplatelets in ethanol. Therefore, in the initial part of the S-isotherm, the adsorption of PEI is easier as concentration rises due to the
cooperative effect and then attains saturation, when no vacant sites remain. At pH 7, the saturation value reaches the highest $\Gamma_{\text{max}}$, i.e. 1.15 mg/m$^2$, whereas at pH 6.5, pH 7.5, pH 8, pH 8.5 and pH 9, the $\Gamma_{\text{max}}$ values are approximately 0.9 mg/m$^2$, 1.09 mg/m$^2$, 0.8 mg/m$^2$, 0.49 mg/m$^2$ and 0.23 mg/m$^2$, respectively.

Figure 4.14. Adsorption isotherm of PEI on the Ag nanoplatelets as a function of suspension pH at various PEI equilibrium concentrations. The maximum adsorption density occurs at suspension pH 7 and is associated with the electrostatic force between the negatively charged Ag surface and the positively charged PEI.
The adsorption density ($\Gamma$) of PEI on the Ag nanoplatelets as a function of suspension pH is shown in Figure 4.14. The decreased adsorption efficiency of the PEI above pH 7 is due to a decrease in the PEI proton association. At pH 6.5, the lower $\Gamma_{\text{max}}$ may result from the higher ionic strength in solution. Therefore, the PEI adsorption on the Ag nanoplatelets had a highest $\Gamma_{\text{max}}$ at suspension pH value of about pH 7.

Figure 4.15 shows the average area occupied by PEI molecules on the surface of Ag nanoplatelets due to adsorption. The occupation area of PEI molecules on the Ag nanoplatelets surface decreases with increase of PEI concentration. At PEI concentration higher than 0.2 wt%, the excess PEI may cause self-aggregation and destabilize the Ag nanoplatelet suspension. To achieve well-stabilized Ag nanoplatelet suspensions, the optimum concentration of PEI is between 0.1 wt% and 0.2 wt%. Using DLVO theory modified for an electrostatic barrier with the thickness of the adsorbed PEI layer, it is possible to calculate the interaction energy curves for the Ag-PEI system. The total interaction energy curves for the Ag nanoplatelets with PEI present at various concentrations in ethanol solution are shown in Figure 4.16. At the distance near the particle surface (< 10 nm), PEI of higher concentrations (i.e. 0.2 wt% and 0.4 wt%) have higher interaction energies than PEI of lower concentrations (i.e. 0.05 wt% and 0.1 wt%) due to a high polyelectrolyte coverage. However, at a distance greater than 10 nm from the particle surface, the total energies of PEI of higher concentrations (i.e. 0.2 wt% and 0.4 wt%) are lower than PEI of lower concentrations (0.05 wt% and 0.1 wt%) resulting from the self-aggregation, and the bridging effect of the excess PEI. The interaction energy curves were calculated using STABIL\textsuperscript{52} and the physical constants listed in
Table 4.2. Appendix B shows the calculation using STABIL to determine the interaction energy as a function of platelet separation distance.

![Graph showing adsorption area of PEI molecules on the Ag nanoplatelets as a function of suspension pH at various PEI equilibrium concentrations.](image)

Figure 4.15. Adsorption area of PEI molecules on the Ag nanoplatelets as a function of suspension pH at various PEI equilibrium concentrations. The occupation area of PEI molecules on the surface of Ag nanoplatelets decreases with the increase of PEI concentration.
Figure 4.16. Total interaction energy curves for the Ag nanoplatelets with PEI at various concentrations in ethanol solution. The curves were calculated by STABIL using flat plate modal.

Table 4.2. List of physical constants used in the calculation of the interaction between Ag nanoplatelets with the present of PEI in pure ethanol.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamaker constant of Ag(^{55,54})</td>
<td>(A_{11} = 16.4 \times 10^{-20} \text{ J}) (A_{131} = 1.7 \times 10^{-20} \text{ J})</td>
</tr>
<tr>
<td>Hamaker constant of ethanol(^{55})</td>
<td>(4.2 \times 10^{-20} \text{ J})</td>
</tr>
<tr>
<td>Lattice constant of Ag</td>
<td>4.0862 Å</td>
</tr>
<tr>
<td>Face diameter of Ag nanoplatelets</td>
<td>55 nm</td>
</tr>
<tr>
<td>Thickness of Ag nanoplatelets</td>
<td>7 nm</td>
</tr>
<tr>
<td>Ag particle surface area</td>
<td>5961 nm(^2)</td>
</tr>
<tr>
<td>Polymer (PEI) thickness on Ag(^{55})</td>
<td>2.8 nm</td>
</tr>
</tbody>
</table>
4.4 Conclusions

High yield (up to 20 g/l) Ag nanoplatelets have been prepared via a POE-water bilayer system by increasing the AgNO₃ concentration. The presence of a bilayer phase field shifted with the increase of AgNO₃ concentration due to the dehydration of the POE head groups. The Ag nanoplatelets synthesized in the POE-water bilayer system had an average thickness of 7 nm, and an average face diameter of 55 nm from a statistical evaluation based on 277 particles. The adsorption isotherms of the PEI on the surface of the Ag tabular nanoparticles reflected the electrostatic interaction of PEI with the Ag nanoplatelets. The characteristic feature of the adsorption isotherms were S-shape with low adsorbability at low PEI equilibrium concentrations, followed by a rapid increase in adsorbability due to cooperative adsorption, and then surface saturation. An individual study on the surface charge properties of the Ag and PEI indicated electrostatic attraction at the PEI/Ag interface during adsorption. At neutral pH, hydroxyl groups on the Ag surface provided the surface-active sites for the maximum adsorption of highly protonated PEI molecules. Adsorption isotherm and the total interaction energy results showed that to disperse Ag nanoplatelets in ethanol, the optimum concentration of PEI was ~ 0.1 wt%.

4.5 References


Chapter 5

Synthesis of Copper Nanoplatelets

5.1 Introduction

Copper (Cu) nanoparticles have been widely used due to their utility in electronics, catalysts, and thermal conducting.\textsuperscript{1, 2} The challenge has been controlling the size, size distribution and shape of nanoparticles. Various approaches have been undertaken in the past decade to prepare nanoparticles,\textsuperscript{3-17} including the two main approaches employed in chemistry: coprecipitation and chemical reduction. In both methods, a surfactant was used to control the particle growth process. Coprecipitation is typically associated with the thermal decomposition of organometallic precursors.\textsuperscript{18-20} Another major approach for the morphology control of nanoparticles is the chemical reduction in colloidal assemblies.\textsuperscript{11, 21, 22} In this approach, the shape of the nanoparticles is partially controlled by the shape of the template. For example, when a reverse micelle is used as the template most of the synthesized particles are spherical. The size of the spherical particles is governed by the application of reverse micelles, the size of which can be controlled by the molar ratio of water: surfactant. Salzmann et al.\textsuperscript{5} controlled morphology of Cu nanoparticles of diameters from 3 to 13 nm using reverse micelles. Song et al.\textsuperscript{12} prepared stable Cu nanoparticles with a diameter of 50 to 60 nm in the organic phases. However, it has been rarely reported for synthesis of controlled anisotropically shaped copper nanoparticles.
In this chapter, morphological control of copper nanoparticles was obtained by chemical reduction in a colloidal self-assembly template. Various parameters are addressed including reduction conditions and nucleation and growth processes. The thermal stability of Cu nanoplatelets was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and a three-stage oxidation effect was observed. The proposed step-wise oxidation procedure provided interesting insight due to the effect of particle morphology.

5.2 Materials and Methods

Copper chloride dehydrate (CuCl$_2$·2H$_2$O, 99 wt%, Aldrich Chemical Co.), copper acetate hydrate (Cu(CH$_3$CO$_2$)$_2$·xH$_2$O, 98 wt%, Aldrich Chemical Co.) and copper nitrate (Cu(NO$_3$)$_2$, 99.999 wt%, Aldrich Chemical Co.) were used as the copper precursors. Aqueous stock solutions of 0.1 M CuCl$_2$, 0.1 M Cu(NO$_3$)$_2$, 0.1 M Cu(CH$_3$CO$_2$)$_2$ and 0.5 M Cu(NO$_3$)$_2$ were prepared using CO$_2$-free deionized water. The CO$_2$-free DI water had been previously prepared by boiling it while flowing argon through the water to remove adsorbed CO$_2$. The removal of CO$_2$ is necessary to limit the formation of copper carbonate during synthesis. Hydrazine hydrate (N$_2$H$_4$·xH$_2$O, reagent grade, Aldrich Chemical Co.) was used as a reducing agent. Polyoxyethylene (C$_{12}$H$_{25}$(OCH$_2$CH$_2$)$_4$OH, POE, Brij 30; Mn ~362, Aldrich Chemical Co.) and ethanol (200 Proof, J. T. Baker Chemicals) were used as-received.

The effect of copper precursor concentration on bilayer template formation was examined before synthesis using the approach described in Chapter 4. The presence of
the birefringence using optical polarized microscopy indicated that at room temperature
the pure bilayer phase formed at POE compositions from 50 wt% to 75 wt% with the 0.1
M and 0.5 M aqueous copper nitrate solutions. The presence of a birefringence as a
function of temperature was examined with a polarized light microscope. No bilayer
phase separation was observed below 60ºC at POE compositions from 55 wt% to 75
wt%, with the presence of the [Cu$^{2+}$] up to 0.5 M. In the current study, with the increase
of [NO$_3^-$] concentration, the dehydration of the POE head group is more severe.
Therefore bilayer phase separation is induced at lower temperature and smaller Cu(NO$_3$)$_2$
concentrations. The marked area in Figure 5.1 illustrates the pure lamellar phase region
with the consideration of both Cu(NO$_3$)$_2$ concentration effect and temperature effect. The
synthesis molar ratio (R) of [water]/[POE] was selected within the marked binary phase
diagram for the POE-water binary system. To minimize the amount of surfactant used in
the synthesis, the R ratio was kept at 13.4 (i.e. 60 wt% POE) for low yield synthesis
using 0.1 M Cu(NO$_3$)$_2$ and higher yield synthesis using 0.5 M Cu(NO$_3$)$_2$ aqueous
solutions.

The reduction of copper nanoparticles was carried out using hydrazine hydrate at
room temperature. Metal reduction generally proceeded according to the following
reaction Eq. (5.1)$^{23}$

$$2Cu^{2+}(aq) + N$_2$H$_4$(aq) + 4OH^- = 2Cu^0(s) + N$_2$(g) + 4H$_2$O \quad E_{cell}^o = 1.50 \text{ V} \quad (5.1)$$

The initial synthesis of copper nanoplatelets was prepared in the POE-water
bilayer system at room temperature. The preparation followed the same steps described
in Chapter 3. A defined amount of aqueous copper stock solution was slowly added to a
specific amount of POE surfactant (R = 13.4). When the POE was mixed with 0.1 M CuCl$_2$, and stirred for 2 mins at ~ 120 rpm, the bilayer phase formed and a translucent blue color was observed. With the reduction of hydrazine, the color of the bilayer phase changed from light blue to dark grey at pH 5 and to brownish yellow at pH 9.5. Excess amount of hydrazine hydrate was added to keep the reduction in an alkaline environment at pH 9.5. The reduced bilayer emulsion was equilibrated for 24 hours before the washing and sample collection. In order to increase the reduction rate, Cu synthesis was also carried out at 55 °C in a thermal bath. The reduced bilayer phase was equilibrated at 55 °C for 1 hour (Figure 5.2). The washing and collection of the as-synthesized powder followed the same procedure for synthesis at room temperature and 55 °C. After equilibrium period, ethanol was used to decompose the bilayer phase in a volume ratio of 10:1. The washing of the Cu nanoplatelets was performed using centrifugation. The Cu nanoplatelets were first centrifuged at 3000 rpm for 5 minutes. The solid particles were then collected and redispersed in ethanol. This washing procedure was repeated three times to remove the surfactant (POE). UV-Vis spectroscopy was used after each wash to monitor the residual concentration of POE. It was verified that after the third wash, no POE absorption peak (at wavelength 221 nm) was observed.
Figure 5.1. Phase diagram of the POE (C₁₂H₂₅(OCH₂CH₂)₄OH) / water system. L₁, micellar solution; L₂, surfactant liquid; Lₐ, lamellar phase; S, solid and W; phases are in equilibrium with water containing a surfactant monomer. Diagram modified from ref.²⁴. The marked area was pure bilayer phase with the addition of 0.1 M Cu(NO₃)₂ and 0.5 M Cu(NO₃)₂ aqueous solutions.
After the final wash, the Cu tabular nanoparticles were dried in air at room temperature for phase identification. Phase identification was performed using an X-ray diffractometer (XRD, Pad V, Scintag, USA) operated at 35 kV and 30 mA with CuKα radiation. The morphologies of the Cu particulates were observed with an atomic force microscope (AFM, MultiMode, Digital Instruments) using Tapping Mode™. The AFM samples were prepared by placing drops of the Cu tabular particles in ethanol on pristine mica substrates. Transmission electron microscopy (TEM, 2010LaB6, JEOL, Japan) was performed at an accelerating voltage of 200 kV. A droplet of ethanolic Cu nanoplatelet suspension was put on a lacy carbon copper grid and dried at room temperature. The weight change and the enthalpy change of the Cu nanoplatelets were determined by

Figure 5.2. The flow diagram used in the synthesis of Cu nanoplatelets. 0.1 M Cu(NO₃)₂, CuCl₂·2H₂O and Cu(CH₃CO₂)₂·xH₂O aqueous solutions were used as a copper precursor for the low yield synthesis with a theoretical yield of 2.4 g/liter. A 0.5M Cu(NO₃)₂ aqueous solution was used for high yield synthesis with a theoretical yield of 12 g/liter.
thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (2960 simultaneous DSC-TGA; TA Instruments Inc., New Castle, DE) in flowing air (100cc/min). To compare the oxidation behavior of platelet particles, TGA-DSC analysis was performed on commercial spherical Cu powder with an average diameter of 1 micron (APS, Alfa Aesar, Ward Hill, MA) in flowing air (100 cc/min).

5.3 Results and Discussion

5.3.1 Reduction of Copper Nanoplatelets

Theoretical \(E_h\)-pH-diagram shows the thermodynamic stability areas of different species in an aqueous solution. Figure 5.3 shows the \(E_h\)-pH diagram of Cu in an aqueous solution at 25°C and 55°C. The stability areas of related species are presented as a function of pH and electrochemical potential scales. Three types of reactions among the species are represented in the diagram: (1) the horizontal lines represent the reactions involving only electron transfer, which is potential dependent; (2) the vertical lines represent the reactions involving only proton transfer, which is pH dependent; (3) the sloped lines represent the reactions having both electron transfer and proton transfer. Synthesis of Cu nanoplatelets was carried out at pH 9.5 in POE-water system with the use of 0.1M and 0.5 M AgNO\(_3\) aqueous solution indicated by the solubility lines in the \(E_h\)-pH diagram of Cu-H\(_2\)O system.
Figure 5.3. Eh-pH-diagram of Cu-H₂O system at 25°C (upper) and 55 °C (lower). The diagram is generated by HSC Chemistry®. Low Eh values represent a reducing environment. High Eh values represent an oxidizing environment. Dashed line a represents the potential of water saturated with dissolved O₂ at 1 atm (above this potential water is oxidized to O₂). Dashed line b represents the potential of water saturated with dissolved H₂ at 1 atm pressure (below this potential water is reduced to H₂). The black dotted line shows the change in the standard redox potential with pH of hydrazine species. The thermodynamic data used in plotting half cell hydrazine redox potential are generated by HSC Chemistry®.
To synthesize base metal materials, the reduction and equilibration of copper nanoparticles are critical steps. The reduction of metal atoms is caused by the transfer of electrons from a reducing agent to the oxidized metallic species. The driving force of the electron transfer is the difference between the standard redox potentials of the two half-cell reactions, $E^\circ_{\text{cell}}$. When $E^\circ_{\text{cell}}$ is positive, the reduction reaction is thermodynamically possible, which also indicates that the redox potential of the reducing agent must have a more negative value than that of the metallic species.

The majority of redox reactions in aqueous solutions involve $H^+$ and $OH^-$ ions. As a result, the pH of the reaction solvent can greatly affect the redox potential of the solutes. Therefore, solution pH can influence the chemistry of the aqueous system and therefore affect the reduction results. A general guideline for metal reduction using appropriate reducing agents and working parameters has been summarized by Goia.$^{27}$ The effect of pH has been aptly illustrated by the redox reaction of hydrazine hydrate, as given in Eq. (5.2).

$$\text{N}_2\text{H}_4 (aq) + 4\text{OH}^- = \text{N}_2(g) + 4\text{H}_2\text{O} + 4e^- \quad (5.2)$$

The $E^\circ$ is $\sim -1.2$ V at pH 14 and decreases to $\sim -0.4$ V at pH 1 without changing the N$_2$H$_4$ concentration, and, as shown in Figure 5.2. Thus, ability of hydrazine to donate electrons is diminished in acidic media. To be used as a reducing agent, hydrazine hydrate should be used in alkaline pH regimes.

With N$_2$H$_4$·xH$_2$O at room temperature, no complete Cu reduction was observed. This is mainly due to the lower electron transfer in the bilayer template than in a solution phase during reduction. Consequently, more rigorous conditions are required to
manipulate the reactivity of the species in the given bilayer-Cu-reducing system. In order to induce further reduction and form Cu°, the system temperature was elevated to increase the reaction rate.

At an increased temperature (i.e. 55 °C), the reduction of N₂H₄ generated a large amount of gas, indicating the formation of N₂ (Eq. 5.1) and therefore a more complete reduction. The color of the bilayer phase changed from brownish yellow to deep brown after 20 minutes, and the system was equilibrated for another 40 minutes at 55°C. When decomposed using ethanol, the color of the bilayer phase was a deep burgundy. The synthesized powder was verified as copper phase by XRD, as shown in Figure 5.4. As shown in Figure 5.5, the particle sizes were classified into three categories: small platelets had an average face diameter of 39 ± 2 nm (± 95% confidence interval, n = 5), an average thickness of 1.8 ± 0.3 nm (± 95% confidence interval, n = 5), and an aspect ratio of ~ 22; medium-size platelets had an average face diameter of 60 ± 2 nm (± 95% confidence interval, n = 5), an average thickness of 4 ± 1 nm (± 95% confidence interval, n = 5), and an aspect ratio of ~ 15; and large platelets had an average face diameter of 98 ± 8 nm (± 95% confidence interval, n = 5), an average thickness of 12 ± 2 nm (± 95% confidence interval, n = 5), and an aspect ratio of ~ 8. The particle morphology determined by the AFM closely aligned with the TEM observations, as shown in Figure 5.6. The associated selected area diffraction (SAD) pattern of a large platelet indicated that the particle was a single crystal parallel to a [111] zone axis.
Figure 5.4. X-ray diffraction pattern of Cu nanoplatelets synthesized in a POE-aqueous bilayer system and reduced by N\textsubscript{2}H\textsubscript{4}·xH\textsubscript{2}O at pH 9.5 and 55 ±1°C (thermal bath) for 1 hour. 0.1 M Cu(NO\textsubscript{3})\textsubscript{2}, used as the Cu source, had a theoretical synthesis yield of 2.4 g/liter.
Figure 5.5. 2-D AFM images of Cu platelets synthesized in a POE-aqueous bilayer system and reduced by $\text{N}_2\text{H}_4\cdot\text{xH}_2\text{O}$ at pH 9.5 and 55 ±1°C (thermal bath) for 1 hour. 0.1M Cu(NO$_3$)$_2$ used as the Cu source had a theoretical yield of 2.4 g/liter. The AFM sample was prepared by placing drops of the ethanolic Cu nanoplatelets on freshly cleaved mica substrate. Tapping Mode™ was used for the AFM analysis.
Figure 5.6. (A) TEM image of Cu platelets synthesized in a POE-aqueous bilayer system and reduced by N$_2$H$_4$·xH$_2$O at pH 9.5 and 55 ±1°C (thermal bath) for 1 hour. The 0.1M Cu(NO$_3$)$_2$ used as the Cu source had a theoretical yield of 2.4 g/liter; (B) TEM image of a Cu nanoplatelet with a large face. The inserted image was obtained by selected area diffraction (SAD), indicating that the particle was a single crystal parallel to a [111] zone axis.
The yield of the Cu synthesis was increased from 2.4 g/l using 0.1 M Cu(NO$_3$)$_2$ to 12 g/l by increasing the concentration of Cu precursor to 0.5 M Cu(NO$_3$)$_2$. Due to its low solubility, 20g/100cc in hot water, Cu(CH$_3$CO$_2$)$_2$ was not suitable as the precursor for a high yield synthesis. As illustrated in Figure 5.7, based on the 95% confidence interval, the AFM of the platelets had an average face diameter of 43 ± 4 nm, an average thickness of 6 ± 1 nm, and an aspect ratio of ~ 7. Figure 5.8 shows both the cumulative and derivative number percent distributions of the thickness and face diameter of 235 high yield Cu nanoplatelets. With the increased concentration of the copper precursor, the synthesized Cu platelets were more uniform in morphology than those synthesized at low precursor concentrations. At an increased feedstock concentration, a higher degree of supersaturation was achieved. A high supersaturation of metal atoms generated a large number of nuclei consuming a major fraction of the metal species in the system. Following their formation, the nuclei undergo rapid growth at the expense of the remaining metal ions in excess of the saturation concentration and form particles. The size of the synthesized particles decreased with the increased number of nuclei initially formed at the high supersaturation. At high supersaturation, particle growth tended to be spontaneous instead of occurring by generations, and therefore the particle size appeared to be more uniform.

Compaction curves of randomly-orientated higher yield (12 g/l) Cu nanoplatelets at room temperature and elevated temperature (200 ºC) are addressed in Appendix C.
Figure 5.7. AFM images of Cu platelets synthesized in a POE-aqueous bilayer system and reduced by N$_2$H$_4$·xH$_2$O at pH 9.5 and 55 ±1°C (thermal bath) for 1 hour. The 0.5 M Cu(NO$_3$)$_2$ used as the Cu source had a theoretical yield of 12 g/liter. With an increased concentration of the copper precursor, the synthesized Cu nanoplatelets were uniform in morphology (compared to Figure 5.5). The Cu nanoplatelets had an average face diameter of 43 ± 4 nm (± 95% confidence interval, n = 5), an average thickness of 6 ± 1 nm (± 95% confidence interval, n = 5), and an aspect ratio of ~ 7. The AFM sample was prepared by placing drops of the ethanolic Cu nanoplatelets on freshly cleaved mica substrate. Tapping Mode™ was used for the AFM analysis.
Figure 5.8. Cumulative and derivative distributions (number%) of thickness and face diameter of high yield Cu nanoplatelets. Based on 235 Cu nanoplatelets synthesized using 0.5 M Cu(NO$_3$)$_2$ as Cu source (R=13.4) in POE-water bilayer system at 55 ±1°C (thermal bath) for 1 hour.
5.3.2 Thermal Stability

To quantify the weight change of the materials during heat treatment, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on higher yield Cu nanoplatelets, as shown in Figure 5.9. When Cu nanoplatelets were heated in air, a ~ 5% weight loss occurred from room temperature to ~145°C, accompanied by an exothermal peak at ~128°C, due to the evaporation of organic molecules absorbed on the surface of the Cu nanoplatelets. A three-stage oxidation occurred from ~145°C to 400°C accompanied by a ~16.4% weight gain. From the calculation, the three-stage weight gain was not a one step stoichiometric reaction (Cu° → Cu₂O or Cu° → CuO), indicating possible phase changes during the oxidation. The Richardson-Ellingham diagram for Cu₂O and CuO is shown in the Appendix D. Peak deconvolution of DSC data by Gaussian area function had four peaks with mean (\( \bar{d} \)) and standard deviation (\( \sigma \)) of: 128, 9.2 (peak 1); 187, 27.1 (peak 2); 243, 19.2 (peak 3) and 307, 23.8 (peak 4). The area ratio of the three exothermal peaks was 1: 0.7: 2.3. Peak deconvolution of the weight gain part of the TGA derivative curve by Gaussian area function had three peaks with mean (\( \bar{d} \)) and standard deviation (\( \sigma \)) of: 187, 22.1 (peak 1); 243, 21.3 (peak 2) and 307, 21.3 (peak 3). Area ratio of the three peaks is: 1: 2.2: 7.5.
Figure 5.9. Thermal stability of high yield Cu nanoplatelets in air. (A) Differential scanning calorimetry (DSC) of Cu nanoplatelets. Peak deconvolution of DSC data by Gaussian area function had four peaks with mean ($\bar{d}$) and standard deviation ($\sigma$) of: 128, 9.2 (peak 1); 187, 27.1 (peak 2); 243, 19.2 (peak 3) and 307, 23.8 (peak 4). The area ratio of the three exothermal peaks was 1: 0.7: 2.3; (B) TGA and the derivative weight change of the Cu nanoplatelets shows the three stage oxidation process. The Cu nanoplatelets were heated at 7 °C/min, and the air flowing rate was 100 cm³/min. Peak deconvolution by Gaussian area function shows three peaks with mean ($\bar{d}$) and standard deviation ($\sigma$) of: 187, 22.1 (peak 1); 243, 21.3 (peak 2) and 307, 21.3 (peak 3). (Area ratio of the three peaks is: 1: 2.2: 7.5. Goodness of fit is $r^2 >0.99$).
DSC-TGA analysis was performed on commercially available copper powder with an average diameter of 1 μm. The oxidation stage of spherical Cu powder was different than the oxidation of Cu nanoplatelets. As shown in Figure 5.10, a significant exothermal peak at ~ 244°C accompanied by a sharp weight gain of ~ 7.21 wt%, and then followed by three small exothermal peaks accompanied by a total weight gain of 13.01 wt% was obtained.

![Figure 5.10. TGA-DSC of commercial spherical Cu powder with an average diameter of 1 micron. Cu powder was heated at 7 °C/min, and the air flowing rate was 100 cm³/min.](image-url)
To investigate the phase change of the as-synthesized Cu nanoplatelets and the commercial copper powders as a function of temperature, XRD analyses were performed after each stage shown in Figure 5.9. Using the TGA-DSC curve (Figure 5.9A), the Cu nanoplatelets were heated at 205°C, 270°C, and 600°C in the same TGA instrument (at the same flow and heating rates) to determine the solid oxidation phase at each stage. XRD results at each stage (Figure 5.11A-C) verified that the weight gain of the 1st-stage (from 150°C to 207°C) and 2nd-stage (from 207°C to 270°C) was mainly due to the oxidation of $4\text{Cu} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{O}$. After the 2nd stage, there was still a large amount of Cu phase in the mixed phase. Compared with XRD results of the 1st-stage oxidation and the 2nd-stage oxidation, the intensities of the CuO phase had no obvious change. The main change was the consumption of the Cu phase, which may be related to two exothermal peaks. After the 3rd-stage (from 270°C to 400°C), all Cu phase was oxidized to CuO. However, as shown in Figure 5.12, after heated at 270°C, the commercial Cu spherical powder is mainly oxidized to form Cu$_2$O phase with small amount of Cu phase remained in the powder mixture. As a consequence, the first significant exothermal peak was mainly due to the reaction of $4\text{Cu}+\text{O}_2 \rightarrow 2\text{Cu}_2\text{O}$, and consumed most of the Cu phase. Therefore, the different oxidation behavior observed between Cu nanoplatelets and the commercial spherical Cu powder was due to the particle morphology effect.
In air, at 205°C

A: Cu₂O, ICDD# 05-0667
B: Cu, ICDD# 04-0836
C: CuO, ICDD# 48-1548

In air, at 270°C

A: Cu₂O, ICDD# 05-0667
B: Cu, ICDD# 04-0836
C: CuO, ICDD# 48-1548
Figure 5.11. XRD analysis of Cu nanoplatelets (high yield sample) heated in air. (A) Heated at 205°, the first stage oxidation of the Cu nanoplatelets was mainly due to the oxidation of $4\text{Cu}+\text{O}_2 \rightarrow 2\text{Cu}_2\text{O}$; (B) Heated at 270°C in air, the second stage oxidation of the Cu nanoplatelets was mainly due to the oxidation of $4\text{Cu}+\text{O}_2 \rightarrow 2\text{Cu}_2\text{O}$; (C) Heated at 600°C in air, after the third stage oxidation, the Cu nanoplatelets were fully oxidized to CuO. The heating rate was 7°C/min and the air flowing rate was 100cc/min.
For the platelet shaped particles, unlike the spherical particles, the atomic structure is partitioned into four categories: (1) the edges of the platelets, (2) the side surfaces of the platelets, (3) the top and bottom surfaces, and (4) the bulk materials of the platelets. Due to the morphology of the higher yield Cu platelets, which had an average face diameter of 43 ± 4 nm and an average thickness of 6 ± 1 nm, a calculation was conducted on the average atom numbers at each morphological partition. (see Appendix E). The atom number ratio of the edge: side surface: top and bottom surface: bulk is 1: 7:
29: 954. That is, each section provides a different number of atoms subject to the oxidation reaction. Therefore, the edges of the platelets might be fully oxidized because of the limited atoms, while the other sections are still undergoing oxidation. Thus the oxidation might follow the sequence of first the edge, and then the side surface, the top and bottom surfaces towards the bulk atoms. The proposed oxidation mechanism reveals an interesting aspect of particle morphology.

5.4 Conclusions

Nanosized Cu platelets were synthesized in a self-assembled POE-water laminar phase region at 55°C. Hydrazine hydrate was used as a reducing agent in an alkali condition to maximize electron donation. An elevated temperature was applied to enhance the reduction reaction rate. A higher yield (12 g/l) of Cu nanoplatelets was synthesized by increasing the Cu(NO₃)₂ concentrations from 0.1 M to 0.5 M. Increasing the feedstock concentration led to a higher degree of supersaturation, and as a consequence, more uniformly distributed particles formed. A three stage oxidation was observed when the as-synthesized Cu nanoplatelets were heated in air. From the DSC analysis, the associated enthalpy ratio with the three oxidation exothermal peaks was 1: 0.7: 2.3. The proposed oxidation procedure revealed an interesting aspect of particle morphology. Based on the average morphology of tabular Cu nanoparticles, the atom number ratio of the edge: side surface: top and bottom surface: bulk was calculated as 1: 7:29: 954. Therefore, oxidation might follow the sequence of edge to side surface to top and bottom surfaces towards the bulk.
5.5 References


Chapter 6

Dispersion of High Yield Copper Nanoplatelets

6.1 Introduction

The most thermodynamically stable phases for metals in aqueous solution are often metal hydroxides.\textsuperscript{1, 2} Copper (Cu), as a transition metal, has a great tendency to form not only metal hydroxide, but metal hydroxyl carbonate or carbonate phases.\textsuperscript{3} Furthermore, the solubility of these “stable” phases can change with the conditions of the medium, especially its pH. Surface corrosion is more severe as particle size decreases towards the nanoscale. A smaller particle size means a higher surface energy, which leads to much easier and faster interactions between the nanoparticles and the liquid medium. Xia et al.\textsuperscript{4} found that Cu nanoparticles with a diameter of 50 nm corroded in distilled water and formed Cu, CuO, Cu(OH)Cl· 2H₂O and Cu₂(CO₃)(OH)₂. In addition, the Cu\textsuperscript{2+} transformation ratio increased much faster for Cu nanoparticles (50 nm) than for micron sized Cu particles (5µm). With environmental issues becoming more prevalent, it is important to investigate a feasible approach to preventing surface degradation while stabilizing nanoparticles in colloidal suspension for further application. To utilize the as-synthesized Cu nanoplatelets (details see Chapter 5) for making continuous film as electrode layer for MLCCs using desired film deposition techniques, Cu nanoplatelets need to be well dispersed in solution. However, the dispersion of Cu nanoplatelets is lack of investigation in the literature.
Two main approaches have been investigated for the successful dispersion of nanoparticulates in liquids: protection-dispersion\textsuperscript{5, 6} and passivation-dispersion\textsuperscript{7, 8}. Protection-dispersion involves the formation of a protective polymer layer or hydrophobic complexes at the metal/water interface.\textsuperscript{9} For example, Wang et al.\textsuperscript{10} were able to prepare stable 30 nm Ag/SiO\textsubscript{2} nanocomposite particles in ethanol-water using the silane coupling agent 3-aminopropyltriethoxysilane combined with the self-assembly system used in the synthesis. Passivation-dispersion involves the formation of sparingly soluble metal salts on the metal/liquid or metal oxide/liquid interface prevent the metal oxidation and/or dissolution. This controls the surface charge and stabilizes nanoparticles.\textsuperscript{3} Chemical surface passivation can be applied to a number of nanoparticles, including ceramics,\textsuperscript{11,12} semiconductors,\textsuperscript{13} and metals.\textsuperscript{14, 15} Solution that affect aggregation (ionic strength, particle charge, and the properties of the dispersants) play an important role in determining the properties of the final dispersion.\textsuperscript{16}

The goals of the current study are to: (1) address the dispersion issues with Cu nanoplatelets in an ethanol-water (7:3 vol\%) co-solvent medium (ethanol was used to remove the excess surfactant from the bilayer system, and the presence of water is required for better pH control.); and (2) investigate the use of oxalic acid and citric acid as dual passivation and dispersion agents to protect Cu nanoplatelets from chemical attack by the co-solvent while providing a surface charge for their dispersion. The behavior of these dual passivation-dispersion agents was evaluated through zeta potential measurements, hydrodynamic diameter distribution measurements, sedimentation experiments and electrostatic deposition. The packing of powders is critical for evaluating the state of a colloidal suspension. A well-stabilized suspension results in a
smooth and continuous green film and vice versa. Electrostatic deposition is a film deposition technique that exploits the Coulombic interactions between oppositely-charged molecules that are physically adsorbed onto a substrate from dilute solutions. It has been shown that this approach can be used to build ordered multilayer films \(^{17,18}\) (of as many as several hundreds of layers) with various combinations of molecular fragments, inorganic and organic layers, biomolecules, photochromic molecules, and conductive polymers.\(^ {19,20}\) In the current work, a single layer of thin Cu film was also deposited from well-dispersed Cu nanoplatelet suspension by electrostatic deposition and film roughness was evaluated.

### 6.2 Materials and Methods

The method used to prepare the Cu nanoplatelets was described in detail in Chapter 5. In brief, 0.5 M copper nitrate (Cu(NO\(_3\))\(_2\), 99.999 wt\%, Aldrich Chemical Co.) aqueous stock solutions were prepared using CO\(_2\)-free deionized water. The CO\(_2\)-free DI water had previously prepared by a process of boiling with flowing argon to remove adsorbed CO\(_2\). CO\(_2\)-free water was used through the experiments. The removal of CO\(_2\) is necessary to limit the formation of copper carbonate during synthesis.

Polyoxyethylene (POE, C\(_{12}\)H\(_{25}\)(OCH\(_2\)CH\(_2\))\(_4\)OH, Brij 30; Mn ~362, Aldrich Chemical Co.) was used as a surfactant, and hydrazine hydrate (N\(_2\)H\(_4\)·xH\(_2\)O, reagent grade, Aldrich Chemical Co.) was used as a reducing agent. Ethanol (200 Proof, J. T. Baker Chemicals) was used as received. An ethanol-water (7:3, vol\%) co-solvent was used in the passivation and dispersion of the Cu nanoplatelets.
Oxalic acid dihydrates (C₂H₂O₄·2H₂O, HOx, Fisher Scientific, Fair Lawn, NJ) and citric acid monohydrate (C₆H₈O₇·H₂O, HCit, 99.5%, Aldrich Chemical Co.) were used as the passivation-dispersion agents. Each was prepared in an ethanol-water (7:3, vol%) co-solvent added in concentrations of 10⁻² M, 10⁻³ M and 10⁻⁴ M with respect to the solids present. Prior to the addition of the Cu nanoparticles, the pH of the solution was adjusted to pH 6.5, pH 7, pH 7.5, pH 8, pH 8.5 and pH 9. These pH adjustments were performed with 0.1 M tetraethyl ammonium hydroxide (TEAOH, Aldrich Chemical, Milwaukee, WI) in an aqueous solution for the 10⁻³ M and 10⁻⁴ M HOx or HCit ethanol-water solutions (7:3, vol%), and a 1 M TEAOH aqueous solution was used for the 10⁻² M HOx or HCit ethanol-water solutions (7:3, vol%). All of the pH measurements were carried out with an ISFET pH probe (Argus IP 65, Sentron Inc., WA) calibrated against the NIST-traceable standards with nominal pH values of pH 4, pH 7 and pH 10.

The bilayer self-assembly phase was formed by mixing POE and a 0.5 M Cu(NO₃)₂ aqueous solution with a molar ratio of water to surfactant, R, equal to 13.4. The Cu²⁺ was reduced to Cu° by the addition of excess hydrazine at pH 9.5. The bilayer microemulsion was equilibrated at 55°C for one hour in a thermal bath during the copper reduction. After equilibration, the newly formed Cu nanoplatelets were washed three times in a pH-adjusted HOx or HCit ethanol-water (7:3, vol%) co-solvent three times at a bilayer: solvent ratio of 1:10.

A droplet of the Cu nanoplatelet suspension was placed on a lacy carbon copper grid and dried at room temperature. Transmission electron microscopy (TEM, 2010LaB6, JEOL, Japan) was performed at an accelerating voltage of 200kV. The interfacial
microstructure of the Cu nanoplatelets in the ethanol-water (7:3, vol%) and the associated microchemistry were studied using a JEOL TEM equipped with a field emission gun (JEOL 2010F) operated at 200 kV. The experimental HRTEM image was recorded with a Gatan slow-scan CCD camera. Electron energy-loss spectrometry (EELS) was performed with a Gatan Enfina parallel electron energy-loss spectrometer attached to the JEOL 2010F microscope. The energy resolution was 1.1 eV measured from the zero-loss peak full width at half maximum (FWHM). A Gatan DigitalMicrograph™ was used to create the HRTEM image and perform the EELS spectral analysis.

The zeta potentials of the Cu nanoplatelets in HOx or HCit as a function of solution pH were determined with a Zeta PALS system (Brookhaven Instruments Corporation, Brookhaven, NY). The Cu nanoplatelet concentration was maintained at 500 ppm for all of the zeta potential measurements at 25°C. The zeta potential distribution results were deconvoluted by a Gaussian area distribution function using PeakFit® (V4.12, Seasolve software Inc., USA). The hydrodynamic diameter distributions (HDDs) of the Cu nanoplatelet suspensions were determined using a quasi-elastic light scattering method on a commercial instrument (Malvern Instruments, Zetasizer Nano S, Malvern Instruments Ltd., UK). The Cu concentrations in the ethanol-water suspension were measured using indirectly coupled plasma atomic emission spectroscopy (ICP-AES, PS3000UV, Leeman Labs, Los Angeles, CA). Standards were made in a mix of ethanol-water (7:3, vol%) to match the matrix of the samples.

Electrostatic deposition was performed using the colloidally-stabilized Cu nanoplatelets in ethanol-water suspension. Prior to deposition, glass substrates were ultrasonically cleaned for five minutes in baths of trichloroethylene, acetone, methanol
and DI water. The glass substrates were then washed in a 1M KOH aqueous solution at pH 10 for 20 seconds, and were then dipped into a 5 wt% polyethylenimine (PEI) aqueous solution with a zeta potential of +24 mV for 20 seconds. The excess PEI was removed by washing in deionized water. The glass substrates were then dipped into the Cu nanoplatelet suspension for 20 seconds and dried in air. The microstructure of the deposited film was observed using atomic force microscopy (AFM) with roughness analysis performed to quantify the nature of the film.

6.3 Results and Discussion

6.3.1 Dispersion Issues for Cu Platelets

TEM was performed on the Cu nanoplatelets after their exposure to the ethanol-water co-solvent solution. Figure 5.5 shows the formation of an amorphous oxide layer on the surface with a thickness of ~3 nm. It is believed that the amorphous phase was a result of the oxidation of Cu from the surface to the bulk solution. The EELS analysis associated with the HRTEM (Figure 6.1) is shown in Figure 5.6. The Cu metal (position 2 in Figure 6.2) has a filled 3d band and shows no sharp white lines, only steps at the two edges and the particle surface. The Cu $L_{23}$ peaks appearing in the CuO spectrum at 931 eV and 950 eV are due to the excitations from the 3 nm amorphous layer near the particle surface (position 1 in Figure 6.2). The double sharp peaks arise through transitions from the 2p core levels to the unoccupied d band. The $L_3$ edge is the transition from the $2p_{3/2}$ level and is separated from the $2p_{1/2}$ transition ($L_2$) edge by the spin-orbit
splitting.\textsuperscript{23} The oxygen $K$ edges resulting from the amorphous oxide layer match the energy-loss values reported by Grunes et al.\textsuperscript{24} Thus, the primary issues with Cu in ethanol-water (7:3, vol\%) are its dissolution and oxidation in the presence of water. It is necessary to passivate the particle surface in order to inhibit this degradation. Therefore, a passivating layer on the surface of the Cu nanoplatelets is needed to provide a barrier against the oxidation of Cu and the dissolution of Cu\textsuperscript{2+} in an aqueous solution.

Figure 6.1. HRTEM micrograph of Cu nanoplatelet showing the amorphous oxide layer with a thickness of $\sim 3$ nm caused by the corrosion of Cu\textsuperscript{2+} on the particle surface. The Cu nanoplatelets were treated in an ethanol-water (7:3, vol\%) co-solvent at pH 6.2. EELS analysis was performed to measure the local chemistry at the amorphous layer (position 1) and the particle surface (position 2); the results verify that the amorphous layer is copper oxide (as shown in Figure 6.2).
Figure 6.2. O $K$-shell and Cu $L_{23}$ edge spectra from copper and copper oxide by EELS analysis on the amorphous oxide phase (position 1 in Figure 6.1) and the particle surface (position 2 in Figure 6.1). The copper metal has a filled $3d$ band and shows no sharp white lines, only steps at the two edges. The Cu $L_{23}$ peaks appearing in the CuO spectrum at 931 eV and 950 eV are due to the excitations from the 3 nm amorphous layer near the particle surface. The double sharp peaks arise through transitions from the 2p core levels to the unoccupied d band. The $L_3$ edge is the transition from the $2p_{3/2}$ level and is separated from the $2p_{1/2}$ transition ($L_2$) edge by the spin-orbit splitting. The oxygen $K$ edges resulting from the amorphous oxide layer match the energy-loss values reported by Grunes et al.
Figure 6.3. (A) A theoretical concentration of the predominance of species of CuO as a function of pH at 25°C. The free energy of formation for the species was determined from the values and equilibrium reactions summarized by Baes and Mesmer. (B) Solubility diagram of CuO as a function of pH at 25°C.
The solubility behavior of copper as a function of pH is likely to be a critical parameter for the dispersion. Figure 5.4 shows a theoretical concentration of the predominance of species of CuO and the theoretical solubility diagram for CuO as a function of solution pH. The minimum solubility for CuO occurs from ~ pH 9.2 to ~ pH 10.5. Below pH 8, the solubility of Cu$^{2+}$ increases with a decrease in solution pH. Furthermore, solubility increases more rapidly with increasing acidity than it does in more alkaline conditions. Therefore, the dissolution of Cu needs to be controlled in the dispersion study by careful control of suspension pH between ~ pH 8 to ~ pH 11.5.

For platelet particles, charge heterogeneity has been explored in clay-water systems. The charge distribution for faces and edges is consistent with crystallographic models for clay in minerals. In a polar solvent, such as water, plate clay particles consist of negatively charged faces and positively charged edges, even though the net electrophoretic charge of the clay particles is negative. The crystal structures at the broken edges of the clay particles are different from those of the flat-layer surface. The direct observation from Thiessen shows that a mixture of a kaolinite sol and a negative gold sol produced gold sol decoration at the edge surfaces of the large kaolinite plates. The electron micrograph of the mixture is shown in Figure 5.7. In the past decade, particle surface charge heterogeneity has been proposed. Recently, in our lab, Kumar et al. have demonstrated that different morphologies of $\alpha$-Al$_2$O$_3$ particles have different isoelectric points (IEPs). As shown in Figure 5.9, $\alpha$-Al$_2$O$_3$ with platelet, columnar, and polyhedral morphologies had IEPs at pH 6.1, 6.8 and 9.8, respectively. The experimental data were consistent with the revised multi-complexation model, calculated based on the proposed model that the IEP values differ with different crystal
habit planes with IEP values for basal plane, prism plane and rhombohedral plane at pH 6.0, pH 8.2 and pH 10, respectively. For platelet shaped particles, the surface charge density of the basal plane dominates the net surface charge, and therefore the platelet particle has an IEP of pH 6.1. In the polyhedron particles, an increased presence of rhombohedral planes increases the IEP pH value to ~ pH 10.

Figure 6.4: Electron micrograph of a mixture of kaolinite and negative gold sol. The negative gold sol decorated at the edge surfaces of the large kaolinite plates, indicating that the plate like clay particles consisted of negatively charged faces and positively charged edges, even though the net electrophoretic charge of the clay particles was negative. Picture taken from ref.28.
The zeta potential of the as-synthesized copper nanoplatelets in an ethanol-water (7:3, vol%) co-solvent showed the coexistence of both positive and negative surface potentials for the platelets. The zeta potential distribution of copper platelets at pH 6 was multi-modal with a major peak at $\sim +20$ mV and a small peak at $\sim -5$ mV (Figure 5.11).

It is possible for metal nanoplatelets to have a charge density variation between the large flat faces and edges. Preliminary work has been performed to evaluate the differential charging effect of the Cu nanoplatelets using an approach analogous to Theissen. Well-dispersed gold (Au) nano-colloids were synthesized through a method adapted from Hauser and Lynn. The prepared gold nanoparticles were spherical in shape with an average hydrodynamic diameter of $\sim 17$ nm and a zeta potential of $-33$ mV. The Au nanoparticle suspension was injected into the Cu bilayer phases after the reduction using

Figure 6.5. The isoelectric point of $\alpha$-alumina varies with its morphology. $\alpha$-Alumina was synthesized by glycothermal synthesis using 1,4-butanediol as a solvent. The solid lines are the surface potential calculated using the revised multi-complexation model, and are consistent with the experimental data. Data taken from ref.30.
Figure 6.6. Zeta potential distribution of Cu nanoplatelets in an ethanol: water (7:3, vol%) co-solvent at pH 6. The Cu nanoplatelets were synthesized in a POE-water bilayer system (\( R = 13.4 \)) with a theoretical yield of 12 g/liter and washed three times in ethanol-water (7:3, vol%). The particle concentration of the Cu nanoplatelets suspension was 500 ppm. The peak deconvolution by the Gaussian area function shows two peaks with a mean \((\bar{d})\) and standard deviation \((\sigma)\) of: -2.7 mV, 4.7 (peak 1); +23.7 mV, 8.9 (peak 2). (Area ratio of the two peaks is: 1:21. Goodness of fit is \( r^2 > 0.992 \).)
hydrazine hydrate to minimize any possible self-agglomeration of the Cu nanoplatelets after the decomposition of the bilayer structure. The Au decorated Cu nanoplatelets were washed three times at ~ pH 6.5 in an ethanol solution containing Au nanoparticles. The concentration of Au nano-spheres in the ethanol was calculated using the physical dimensions of Au nano-spheres and Cu nanoplatelets and assuming that the edges of the Cu nanoplatelets were covered by the Au spheres. TEM performed on the Au and Cu nanoplatelet mixture after the final wash (Figure 6.7) revealed a tendency of the Au nano-spheres to be located on the edges of the Cu nanoplatelets, but no clear-cut Au decoration on their surfaces was apparent. There is no enough evidence to support that the Cu nanoplatelets have a positive charge on the planar face and a negative charge along the edges. The surface state of Cu nanoplatelet is more complicated than that of classical clay platelet particles, which have a specific crystal habit. The synthesized Cu nanoplatelets are not single crystals. When the big face of the Cu nanoplatelets has a positive charge, the edge might carry positive, negative or neural charges. Therefore, nine possible heterogeneities combinations might exist (i.e. $C_3^1 \cdot C_3^1 = 9$) associated with suspension pH. There are a large number of possibilities for differential charge on metal nano-platelets and consequently self-aggregation modalities. Therefore, screening the charge heterogeneity of the Cu nanoplatelets and forming a passivation layer with uniform negative charge via passivation-dispersion permits better control over the surface charge activity, which can simplify the dispersion scheme.
Figure 6.7. TEM image of Cu nanoplatelets mixed with Au nanoparticles at pH 6.5 in an ethanol-water (7:3, vol%) solution. The suspension pH was adjusted by 0.1 M TEAOH in an aqueous solution. The Cu nanoplatelets were synthesized by a POE-water bilayer system at room temperature (R= 13.4). 0.5 M Cu(NO₃)₂ used as the Cu precursor has a theoretical yield of 12 g/liter. Well-dispersed gold (Au) nano-spheres with a diameter of ~ 15 nm and a zeta potential of -33 mV were synthesized through an adaptation of the method proposed by Hauser and Lynn. No obvious pattern of Au decoration is apparent on the surface of the Cu nanoplatelets.
6.3.2 Passivation-Dispersion

To protect the metal surface from chemical degradation by the ethanol-water co-solvent, and shield the charge heterogeneity on the surface of the Cu nanoplatelets, a passivation approach was used to form a sparingly soluble salt with the available Cu\(^{2+}\)(aq). Both oxalic acid (HOx) and citric acid (HCit) were selected as candidate passivation agents. The criteria for passivation is (1) the formation of a strong metal-ligand bond at the surface; (2) little or no effect on the solubility of the passivation agent on the solubility of the metal; and (3) provide suitable charge/surface potential combined with low ionic strength for dispersion of the metal nanoplatelets.\(^7\)

6.3.2.1 Passivation-Dispersion by Oxalic Acid.

Oxalic acid (HOx) was chosen as a potential passivation agent because Cu\(^{2+}\) ions near the particle surface react with the oxalate ions to form a copper oxalate complex with an extremely low solubility (1.6 × 10\(^{-4}\) M at 18\(^{\circ}\)C)\(^{37}\) on the particle surface. The first attempt to disperse the Cu platelets was carried out using 10\(^{-2}\) M and 10\(^{-3}\) M HOx in an ethanol-water (7:3,vol\%) co-solvent to wash the Cu nanoplatelets after template-directed synthesis in the POE-water bilayer system. Ethanol was used to remove the excess surfactant from the bilayer system, and the presence of water is required for better pH control. The zeta potential of the Cu nanoplatelets as a function of pH in ethanol-water with and without the protection of HOx was measured. As shown in Figure 6.8, the IEP of Cu nanoplatelets in ethanol-water (7:3, vol\%) is ~ pH 7.3. The addition of 10\(^{-3}\) M HOx shifted the IEP of the Cu nanoplatelets towards the acidic region (~ pH 5.2) and
slightly increased mean zeta potential to -15 mV at a pH above pH 7. The addition of 10^{-2} M HOx further increased the mean zeta potential of the Cu platelets to a magnitude greater than -35 mV at a pH above pH 5. For both HOx concentrations above pH 5, the surface charge of the Cu nanoplatelets becomes independent of the suspension pH. The effect of HOx concentration on the conductivity of the Cu nanoplatelets is shown in Figure 6.9. The primary result of using 10^{-2} M HOx was that it had a high conductivity of 396 μS/cm. Therefore, the high ionic strength compressed the double layer and might be a contributing factor to the suspension instability. The high concentration of the electrolyte resulted in a small interparticle separation distance before the repulsion force between the particles became negligible.

The zeta potential distribution of the Cu nanoplatelets with the addition of 10^{-2}M HOx at pH 9 was tri-modal, as shown in Figure 6.10. Deconvolution of the peak using the Gaussian area distribution function reflected three discrete peaks with a mean ($\bar{\eta}$) and standard deviation ($\sigma$) of: -54 mV, 5.2 (peak 1); -37 mV, 5.8 (peak 2) and -10 mV, 3.9 (peak 3). (The area ratio of the three peaks is: 1.2: 12.3: 1. The goodness of the fit is $r^2 > 0.995$.) Despite the small percentage of low zeta potential (~11mV) surfaces, they are likely the main cause of agglomeration at pH 9.
Figure 6.8. Zeta potential of Cu nanoplatelet suspensions as a function of pH with and without the addition of oxalic acid in ethanol-water (7:3, vol%). The pH values were adjusted with 1M TEAOH in water. The particle concentration of the Cu nanoplatelets suspension was 500 ppm. The error bars are based on a 95% confidence interval (n = 5). The shift in the IEP of the Cu nanoplatelets after the addition of oxalic acid is due to the specific adsorption of oxalate.
Figure 6.9: The conductivity of Cu nanoplatelet suspensions as a function of pH with the addition of oxalic acid (HOx) in ethanol-water (7:3, vol%). 1 M TEAOH in an aqueous solution was used to adjust the suspension pH. Ionic strength is proportional to conductivity. Therefore, $10^{-2}$ M HOx had much higher ionic strength than the $10^{-3}$ M HOx solution. The high ionic strength compressed the double layer of Cu nanoparticles, resulting in an un-stabilized Cu nanoplatelet suspension.
The hydrodynamic diameter distribution of the Cu nanoplatelet suspension after three washing iterations in a $10^{-2}$ M HOx ethanol-water (7:3, vol%) co-solvent at pH 9 was measured as a function of sedimentation time by quasi-elastic light scattering technique (QELS). The QELS technique relies on measuring the Brownian motion of small particles and relating this to the hydrodynamic diameter based on the assumption that particles are spheres.\(^{38}\) For non-spherical particles, the hydrodynamic diameter

Figure 6.10. Zeta potential distribution of Cu nanoplatelets in $10^{-2}$ M oxalic acid at pH 9. The Cu nanoplatelets were negatively charged. Peak deconvolution by the Gaussian area function shows three peaks with a mean ($\bar{d}$) and standard deviation ($\sigma$) of: -54 mV, 5.2 (peak 1); -37 mV, 5.8 (peak 2) and -10 mV, 3.9 (peak 3). (The area ratio of the three peaks is: 1.2: 12.3: 1. The goodness of the fit is $r^2 > 0.995$.)
would be based upon the sphere which has the same average diffusion coefficient as that of the particles. As shown in Figure 6.11, the Cu nanoplatelets with a solid loading of 1000 ppm had a unimodal distribution with a mean hydrodynamic diameter of ~ 42 nm at the initial stage. Agglomerates started to form in ~2 hours and the hydrodynamic diameter distribution became bimodal. The Cu nanoplatelet suspension became less stable in the next hour, and the hydrodynamic diameter distribution is also bimodal, but shifted toward larger diameter.

![Graph showing hydrodynamic diameter distribution](image). Figure 6.11. Hydrodynamic diameter distribution of Cu nanoplatelet suspensions after three washes in a 10⁻² M oxalic acid ethanol-water (7:3, vol%) at pH 9. The suspension pH was adjusted by a 1 M TEAOH aqueous solution. Cu nanoplatelets cannot be stabilized in 10⁻² M oxalic acid.
At a low HOx concentration (i.e. 10^{-3} M), when the pH > pH 7, the HOx may dissociate in water to produce negatively charged carboxylate ions, which can form a sparingly soluble copper oxalate CuC_2O_2. The pKa values of HOx are pKa_1 = 1.27 and pKa_2 = 4.28. The negative charge from the carboxylic ions provides a negatively charged particle surface. The magnitude of the surface charge is relatively low (-15 mV), not high enough to overcome the attractive force between particles. After the HOx concentration is increased to 10^{-2} M, the excess free carboxylate sites greatly increase the magnitude of the surface charge to ~ -40mV. However, the high ionic strength compressed the double layer resulted in the destabilization of Cu nanoplatelet suspension. The morphology of the Cu nanoplatelets dispersed in a 10^{-2} M HOx ethanol-water (7:3, vol%) co-solvent at pH 9 is shown in Figure 6.12. The surface of the Cu nanoplatelets is covered by a passivation layer (~ 4 nm), which is believed to be a sparingly soluble copper oxalate. The high concentration of HOx leads to an excess amount of HOx precipitated among Cu nanoplatelets. The control of HOx concentration is therefore of great importance in the passivation and dispersion of Cu nanoplatelets. Excess HOx may remove more Cu ions from the particle surface and increase the ionic strength of the suspension.

6.3.2.2 Passivation-Dispersion by Citric Acid.

Citric acid (HCit) plays an important role as a ligand for transition metal ions in chemical reactions of both biological and analytical interest. The ligand has been
applied as a masking agent for most metal ions, preventing the precipitation of these ions as hydroxides or other slightly soluble salts.\textsuperscript{42}

Figure 6.12. TEM micrographs of Cu nanoplatelets washed three times in a 10\textsuperscript{-2} M oxalic acid ethanol-water (7:3, vol\%) co-solvent at pH 9. The suspension pH was adjusted by 1 M TEAOH in an aqueous solution. The Cu nanoplatelets were synthesized in a POE-water bilayer system (R = 13.4). 0.5 M Cu(NO\textsubscript{3})\textsubscript{2} when used as a Cu precursor has a theoretical yield of 12 g/ liter. The bridges present among the Cu nanoparticles are due to the colloidal instability of the oxalate-treated Cu nanoplatelets.
In the current study, HCit was used to passivate the surface of the Cu nanoplatelets by forming copper citrate on the Cu surface\textsuperscript{43}. ICP-AES analysis of the suspension supernatant was performed to investigate the passivation with $10^{-3}$ M HCit at pH 8 in terms of a relatively constant solubility due to the formation of a sparingly soluble copper citrate on the surface. ICP-AES shows that the concentration of $\left[ \text{Cu}^{2+} \right]$ in an ethanol-water (7:3, vol\%) co-solvent system is less than $4 \times 10^{-4}$ M, indicating that the Cu$^{2+}$ concentration in the solution is negligible.

As shown in Figure 6.13, with the addition of $10^{-4}$ M citric acid, the zeta potential of the Cu nanoplatelets increased to the magnitude of -15 mV, which was independent of the suspension pH. When the concentration of HCit was increased to $10^{-3}$ M, the zeta potential of the Cu nanoplatelets increased in magnitude to -25 mV at a pH above pH 8, at which point the zeta potential was independent of the suspension pH. At room temperature, a zeta potential with magnitude greater than $\pm$ 25 mV is generally necessary to produce a stable dispersion in a low to moderate ionic strength suspension\textsuperscript{44}. When the magnitude of the zeta potential was high enough to provide a stable dispersion, the dispersion could be achieved by use of HCit alone.

The zeta potential distribution of the Cu nanoplatelets with the addition of HCit had a uni-modal distribution, as shown Figure 6.14. With an increase of the HCit concentration from $10^{-4}$ M to $10^{-3}$ M, the surface charge became homogeneous. At pH 8.5, the Cu nanoplatelets were negatively charged when passivated with $10^{-3}$ M HCit. The electrostatic force that counteracted the attraction due to van der Waals force was large enough to overcome the attraction between the Cu nanoparticles. The effect of HCit concentration on the conductivity of the Cu nanoplatelets is shown in Figure 6.15.
As the conductivity of HCit is lower than 80 µS/cm, stabilization of Cu nanoplatelet suspension occurs in an alkaline solution, as was determined later in sedimentation experiment results. Therefore, HCit can be used as a successful dual passivation-dispersion agent in ethanol-water (7:3, vol%).

Figure 6.13. Zeta potential of Cu nanoplatelet suspension as a function of pH with and without the addition of citric acid ethanol-water (7:3, vol%). The suspension pH values were adjusted by a 1M TEAOH aqueous solution. The error bars are based on a 95% confidence interval (n = 5).
Figure 6.14. Zeta potential distribution of Cu nanoplatelets in an ethanol-water (7:3, vol%) co-solvent at pH 8.5. The Cu nanoplatelets were synthesized in a POE-water system with a theoretical yield of 12 g/liter. The Cu nanoplatelets were washed three times in $10^{-3}$M HCit or a $10^{-4}$ M HCit ethanol-water (7:3, vol%) co-solvent, respectively. With the addition of $10^{-3}$ M citric acid, the surface charge of the Cu nanoplatelets became negative.
Figure 6.15. Conductivity of Cu nanoplatelet suspensions as a function of suspension pH with the addition of HCit in ethanol-water (7:3, vol%). 1M TEAOH in an aqueous solution was used to adjust the suspension pH. Ionic strength is proportional to conductivity.
Gravitational sedimentation of the Cu nanoplatelet suspensions (1000 ppm) was performed in the presence of $10^{-3}$ M HCit as a function of pH, from pH 6 to pH 9. In general, particles in a dilute coagulated suspension settle rapidly in bulk, and the supernatant is clear; the sediment has a relatively low packing density and is easily redispersed. Particles in a well-dispersed suspension settle relatively slowly and the sediment is more dense and less easily dispersed.\(^{38}\) The sedimentation behavior of the dispersion depends on a number of factors including the degree of dispersion and the dispersion stability.\(^ {45}\) Sedimentation tests are easily carried out and yield direct information for evaluating the state of dispersion. As shown in Figure 6.16, well-dispersed Cu nanoplatelet suspensions were observed at above pH 8 in ethanol-water (7:3, vol%). The Cu nanoplatelets retained a unimodal hydrodynamic diameter distribution after 4 days (Figure 6.17) before slow flocculation was observed. Initial electrostatic deposition was carried out using a Cu nanoplatelet suspension well dispersed by $10^{-3}$ M HCit in ethanol-water (7:3, vol%). Packing the powders also reflects the dispersion state of the suspension. The structure of the green body depends on the processing technique and conditions.\(^ {46}\) If particles are well-dispersed, the deposited film should be smooth and continuous without obvious aggregates, and vice versa. As shown in Figure 6.18, at pH 8.5, a single layer of Cu platelets formed on the glass substrate within 20 seconds. The thickness of the as-deposited film was 22 nm, with a surface roughness (root mean square) of 2.5 nm.
Figure 6.16. Sedimentation observation of Cu nanoplatelet suspensions as a function of pH after 120 hours (5 days). The nanoplatelets were washed in a $10^{-3}$ M citric acid ethanol-water (7:3) co-solvent three times and then pH adjusted by 1 M TEAOH in an aqueous solution. The Cu nanoplatelet suspensions show a high stability in the alkaline region from pH 8.0 to pH 9.0.

Figure 6.17. Hydrodynamic diameter distribution of a Cu nanoplatelet suspension dispersed in $10^{-3}$ M citric acid ethanol-water (7:3, vol%) at pH 8.5. Four days after the sedimentation experiment shown in Figure 6.17. The pH was adjusted by a 1M TEAOH aqueous solution.
Figure 6.18. AFM 3-D image of Cu film made by electrostatic deposition. The Cu suspension was washed three times using $10^{-3}$ M HCl ethanol-water (7:3, vol%) solution at pH 8.5. The thickness of the Cu film is 22 nm with a surface roughness (RMS) of 2.5 nm.
Citric acid (HCit) is a tricarboxylic acid with pKa₁ = 3.13, pKa₂ = 4.76 and pKa₃ = 6.40. As pH increases, the tricarboxylic acid successively releases protons, producing negative carboxylate ions. Because of its three carboxylate groups, the concentration of HCit needed to provide the same magnitude of charge is significantly lower than that required for oxalate. In the alkaline region, the [Cu₂(C₆H₆O₇)₂] complex is the predominant species, in which two carboxylate ions can complex with the Cu sites on the surface of the particle. The third carboxylic group and the hydroxyl group increase the negative surface charge of the Cu nanoplatelets. [Cu₂(C₆H₆O₇)₂] is the predominant complex with a molar ratio of 1:1 between Cu (II) and citric ions, as the existing literature supports. The [Cu₂(C₆H₄O₇)₂] complex is the most favorable form, with a formation stability constant above 10¹⁴ from pH 2 to pH 11. Because of the steric hindrance from the branched HCit structure, the Cu nanoplatelet suspension dispersed in 10⁻³ M HCit had a higher stability than that dispersed by HOx. The thickness of the HCit and HOx layer was estimated from the 3-D representative structure of the respective molecules using ACD ChemSketch. Figure 6.19 shows the space filling models for both HCit and HOx. The total interaction energy curves of Cu nanoplatelets dispersed in 10⁻³ M HCit and 10⁻² M HOx were plotted in Figure 6.20. It is shown that with the presence of 10⁻³ M HCit, the stability of Cu nanoplatelet suspension is increased from an unstable system to a metastable system. The coagulation is expected to occur slowly in a metastable system.
Figure 6.19. Space-filling models of (A) citric acid and (B) oxalic acid molecules. The 3-D structures were drawn using ACD ChemSketch™. The estimated spherical diameters for citric acid and oxalic acid are 0.70 nm and 0.37 nm, respectively, as determined by ACD ChemSketch™ output.
6.4 Conclusions

The question underlying the current work has been whether it is possible to recover chemically synthesized colloidal Cu nanoparticles in a well-dispersed state. It has been demonstrated that the addition of citric acid (HCit) creates a uniform negative
charge on the surface of Cu nanoplatelets. The uniform negative charge results from the formation of a citrate complex on the particle surface. The copper citrate complex acts as a passivating agent to protect the surface from degradation by the ethanol-water (7:3 vol%) environment. The negative charge provided by the passivation layer is independent of the solution pH. Passivation allows for more control over the surface activity, which can simplify the resulting dispersion scheme. Well-dispersed Cu nanoplatelet suspensions were obtained using $10^{-3}$ M HCl at a pH above pH 8 as observed in sedimentation and green film deposition experiments. For the purpose of comparison, the application of oxalic acid (HOx) as a passivation-dispersion agent was also investigated in the same system. Some possible charging mechanisms for HCl and HOx have been discussed according to surface charge, ionic strength and their carboxylic acid properties. In conclusion, a passivation-dispersion approach provides excellent control of colloid stability on Cu nanoplatelets in ethanol-water (7:3, vol%).

6.5 References


Chapter 7

Synthesis of Nickel Nanoplatelets and Copper/Nickel Nanoplatelets

7.1 Introduction

The demand for multilayer ceramic capacitors (MLCCs) has rapidly increased in the past decade due to the rapid growth in the number of cellular phones, and computers.\(^1\) In the manufacturing of MLCCs with a smaller size, higher performance and lower cost, the development of a base metal internal electrode (BME) and thinner dielectric ceramic layers have become critical issues.\(^2\)\(^-\)\(^5\) Physical properties for various electrode materials of MLCCs are shown in Table 7.1. Nickel (Ni),\(^3\)\(^,\)\(^6\)\(^,\)\(^7\) copper (Cu)\(^8\) and Cu/Ni bimetallic alloy\(^9\) are good candidates for the BME in MLCCs because of their low cost, good conductivity and high melting temperatures.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Melting Point (°C)</th>
<th>Resistivity (mΩ)</th>
<th>Density (kg/m(^3))</th>
<th>Firing Atmosphere</th>
<th>Price Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>961</td>
<td>1.62</td>
<td>10.50</td>
<td>Air</td>
<td>3</td>
</tr>
<tr>
<td>Cu</td>
<td>1080</td>
<td>1.72</td>
<td>8.96</td>
<td>Reducing</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td>1453</td>
<td>6.9</td>
<td>8.902</td>
<td>Reducing</td>
<td>1</td>
</tr>
<tr>
<td>Pd</td>
<td>1552</td>
<td>10.4</td>
<td>12.02</td>
<td>Air</td>
<td>80</td>
</tr>
</tbody>
</table>
Ni nanoparticles have been prepared by various methods, including chemical reduction,\textsuperscript{10-12} electrochemical technique,\textsuperscript{13} microemulsion,\textsuperscript{14-16} and microwave.\textsuperscript{17} An elevated temperature and the introduction of nucleating agents are always used in the Ni synthesis to increase the nucleation rate. Hedge et al.\textsuperscript{11} have found that the reduction of Ni from Ni(OH)$_2$ is ten times faster in the presence of Pt or Pd. During the reduction, the metal species with a higher redox potential precipitate first, followed by the coprecipitation of the second component.\textsuperscript{18} The effectiveness of heterogeneous nucleation is determined mainly through the crystallographic nature of the surfaces between the nucleating agent and the second component. Based on the Turnbull-Vonnegut theory,\textsuperscript{19} if the lattice structure on the surface of the agent is identical to that of the forming crystal, the interface between the two will be coherent. The interfacial energy between the nucleus and the catalytic surface element is at a minimum when the nucleus forms coherently. If there is a lattice mismatch between the two phases, the nucleus is not coherent but has a disregistry, $\delta$, which is given by Eq. (7.1)\textsuperscript{19}

$$\delta = \left| \frac{x - a_o}{a_o} \right|$$

(7.1)

where $a_o$ and $x$ are the lattice parameters of the nucleus in the strain-free and strained conditions. It has been determined experimentally that the degree of misfit affects the energy barrier to heterogeneous nucleation in qualitative agreement with the Turnbull-Vonnegut theory. Therefore, the formation of precipitates is expected to be catalyzed by the nucleating agent, one criterion of the effectiveness being the lattice match between the two phases.\textsuperscript{20}
In this chapter, synthesis of Ni nanoplatelets in POE-water bilayer system has been investigated. As shown in the POE-water binary phase diagram (Figure 5.1), to maintain POE-water self-assembled lamellar structure, synthesis temperature needs to be controlled below ~ 60°C. With the temperature constraint, synthesis of pure phase Ni was conducted with the application of nucleating agents. By heterogeneous nucleation at 55°C, Ni nanoplatelets with a face diameter of 36 ± 5 nm and thickness of 8 ± 1 nm were obtained by the application of Pd at a molar ratio of $5 \times 10^{-2}$ Pd/Ni. Cu$_{0.81}$/Ni$_{0.19}$ bimetallic nanoplatelets have also been synthesized in the same system using Cu as the nucleating agent.

### 7.2 Materials and Methods

Nickel chloride (NiCl$_2$; A.C.S reagent grade, Aldrich Chemical Co.) was used as a nickel source. Silver nitrate (AgNO$_3$; A.C.S. reagent grade, Aldrich Chemical Co.), copper nitrate (Cu(NO$_3$)$_2$, 99.999 wt%, Aldrich Chemical Co.) and palladium nitrate (Pd(NO$_3$)$_2$, >99 wt%, Aldrich Chemical Co.) were used as nucleating agents for the nickel synthesis. CO$_2$-free deionized water was used for the synthesis, and prepared by boiling it with flowing argon to remove adsorbed CO$_2$. The removal of CO$_2$ is necessary to limit the formation of carbonate during synthesis. Polyoxyethylene (POE, C$_{12}$H$_{25}$(OCH$_2$CH$_2$)$_4$OH, Brij 30; Mn ~362, Aldrich Chemical Co.), hydrazine hydrate (N$_2$H$_4$·xH$_2$O; reagent grade, Aldrich Chemical Co.) and ethanol (200 Proof, J. T. Baker Chemicals) were used as received.
NiCl₂ was used as the nickel source based on a previous study by Yener²¹ that the nitrate in Ni(NO₃)₂ is an oxidizing agent more resistant to reduction. The procedure illustrated in the flow chart in Figure 7.1 was used to prepare Ni nanoparticles in the bilayer system. The particles were synthesized by the co-precipitation method. A typical synthesis used 19 ml 0.04 M NiCl₂ (aq.) with 0.9 ml of 0.04 M AgNO₃, 0.04 M Cu(NO₃)₂ or 0.04 M Pd(NO₃)₂ in a molar ratio of nucleating agent/Ni equaled to 5×10⁻². The mixed aqueous solution was slowly added to 30 ml POE surfactant to form a self-assembled bilayer phase with a [surfactant]/[water] molar ratio of 13.4. Excess H₂N₄ was added to the washing solution to keep the pH above 9. This step was followed by the reduction at 55°C and the temperature was controlled by a thermal bath. In terms of different nucleating agents, the reduced bilayer phase was equilibrated at 55°C for various periods of time. The Ni particles were recovered by a solvent extraction process, in which the bilayer Ni-POE system was washed four times in an ethanol solution by centrifugation.

The solid phase was characterized using an X-ray diffractometer (XRD, Pad V, Scintag, USA) operated at 35 kV and 30 mA with CuKα radiation. Chemical purity was characterized by energy-dispersive spectroscopy (EDS) equipped on secondary electron microscopy (SEM, Hitachi H3500N, Japan). Hot-stage XRD was performed on the synthesized solid phases by heating to 500°C in ultra high purity N₂ with the O₂ content below 2 ppm and under a vacuum (10⁻⁵ bar). The morphologies of the Ni particulates were observed by atomic force microscope (AFM, MultiMode, Digital Instruments) using Tapping Mode™. The AFM samples were prepared by placing drops of the ethanolic Ni tabular particles on pristine molecularly cleaved mica substrates. Transmission electron microscopy (TEM, 2010LaB6, JEOL, Japan) was performed at an accelerating voltage of
200kV. A droplet of Ni nanoplatelet ethanol suspension was dropped on a holey carbon copper grid and dried at room temperature.

![Flow chart illustrating the procedure used in the synthesis of Ni tabular particles via the chemical reduction method.](image)

Figure 7.1. Flow chart illustrating the procedure used in the synthesis of Ni tabular particles via the chemical reduction method. AgNO₃, Pd(NO₃)₂ and Cu(NO₃)₂ are used as the nucleating agents due to their crystal structures, which are identical to that of Ni.

7.3 Results and Discussion

7.3.1 Reduction of Ni Nanoplatelets

Figure 7.2 shows the potential-pH diagram of Ni in an aqueous solution. In an open circuit condition, NiO is the predominant species over a wide pH range from above pH 4 to highly alkaline pH values. The stable area for Ni phase exists in a narrow region
below pH 4. Nickel (Ni) is significantly less noble than copper and much less noble than silver and other noble metals. As shown in Eq. (7.2),\textsuperscript{22} with the reduction of N\textsubscript{2}H\textsubscript{4}·xH\textsubscript{2}O the magnitude of the standard redox potential (\(E^\circ\text{cell} = 0.25\) V for all values greater than \(\sim\)pH 4) is lower than that of Cu reduction with hydrazine (Figure 5.3, \(E^\circ\text{cell} = 1.50\) V for all values greater than \(\sim\)pH 3.5). Therefore, a nucleating agent is introduced to promote Ni phase formation in the POE-water bilayer system to decrease the free energy barrier and promote nickel formation using heterogeneous nucleation.

\[
2\text{Ni}^{2+} (aq) + \text{N}_2\text{H}_4 (aq) + 4\text{OH}^- = 2\text{Ni}^0 (s) + \text{N}_2 (g) + 4\text{H}_2\text{O} \quad E^\circ\text{cell} = 0.92\text{V} \tag{7.2}
\]

Figure 7.2. Eh-pH-diagram of the Ni-H\textsubscript{2}O system at 55\(^\circ\text{C}\). The Eh-pH-module is based on STABCAL - Stability Calculations for Aqueous Systems - and the diagram was generated by HSC Chemistry\textsuperscript{®} for Windows.\textsuperscript{23} The black dotted line shows the change in the standard redox potential with pH of hydrazine species. The thermodynamic data used in plotting half cell hydrazine redox potential are generated by HSC Chemistry\textsuperscript{®}.
Palladium (Pd), silver (Ag) and copper (Cu) were considered to be potential nucleating agents for Ni nanoplatelets synthesis due to their crystal structures (FCC), which are identical to that of Ni. In addition, Pd, Ag and Cu are commonly used electrode materials for MLCCs; their presence in the Ni synthesis will not affect the Ni being used in the same application. As listed in Table 7.2, Pd has a lattice parameter of 3.8902Å, which results in a 10% lattice mismatch with Ni. Ag has a lattice parameter of 4.0862Å, which has a 16% lattice mismatch with Ni, and Cu yields the minimum lattice mismatch (3%) with Ni.

Table 7.2. Crystallographic parameters of potential nucleating agents for Ni synthesis. Disregistry between Ni and the nucleating agent was calculated by Eq. (7.1).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Crystal structure</th>
<th>Lattice parameter (Å)</th>
<th>Lattice mismatch% with Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>3.5238</td>
<td>N/A</td>
</tr>
<tr>
<td>Pd</td>
<td>FCC</td>
<td>3.8902</td>
<td>10%</td>
</tr>
<tr>
<td>Ag</td>
<td>FCC</td>
<td>4.0862</td>
<td>16%</td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>3.6150</td>
<td>3%</td>
</tr>
</tbody>
</table>

A brief summary of the Ni synthesis results is listed in Table 1.1. With the use of a small amount of Pd as the nucleating agent, the bilayer phase had a light lavender color immediately after the reduction by N₂H₄. At 55°C, the Ni#5 started changing color, to grey in 30 minutes and deep grey in the next 40 minutes. After additional equilibration for another 30 minutes, the Ni particles were washed in an ethanol solution. As shown in the XRD analysis (Figure 7.3), the Ni#5, which had a 5×10⁻² molar ratio of Pd/Ni, resulted in the reduction from NiCl₂ to a Ni phase. The rest of the samples (Ni #1 to Ni #4) showed incomplete Ni reduction. And the synthesis results are discussed in more
detail in Appendix F. Therefore, the Ni nanoplatelet synthesis in POE-water bilayer system showed that to obtain complete Ni reduction in POE-water bilayer system with the temperature constraint (below 60°C), the minimum amount of Pd needed was 5 mol% with the respect to Ni.

Table 7.3. Brief summary of experimental conditions for Ni synthesis using Pd(NO$_3$)$_2$, AgNO$_3$, and Cu(NO$_3$)$_2$ as the nucleating agents. Disregistry between Ni and the nucleating agent was calculated by Eq. (7.1).

<table>
<thead>
<tr>
<th>Nucleating agent</th>
<th>Disregistry with Ni</th>
<th>Sample #</th>
<th>Nucleating agent/Ni molar ratio</th>
<th>Time/mins (55°C)</th>
<th>pH</th>
<th>XRD Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(NO$_3$)$_2$</td>
<td>10%</td>
<td>Ni#1</td>
<td>$1 \times 10^{-2}$</td>
<td>120</td>
<td>9.5</td>
<td>Ni &amp; Unknown</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni#2</td>
<td>$2 \times 10^{-2}$</td>
<td>120</td>
<td>9.7</td>
<td>Ni &amp; Unknown</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni#3</td>
<td>$3 \times 10^{-2}$</td>
<td>120</td>
<td>9.9</td>
<td>Ni &amp; Unknown</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni#4</td>
<td>$4 \times 10^{-2}$</td>
<td>120</td>
<td>10.0</td>
<td>Ni &amp; Unknown</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni#5</td>
<td>$5 \times 10^{-2}$</td>
<td>100</td>
<td>10.5</td>
<td>Ni</td>
</tr>
<tr>
<td>AgNO$_3$</td>
<td>16%</td>
<td>Ni#6</td>
<td>$1 \times 10^{-2}$</td>
<td>600</td>
<td>10.9</td>
<td>No Ni</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni#7</td>
<td>$2 \times 10^{-2}$</td>
<td>600</td>
<td>9.7</td>
<td>No Ni</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni#8</td>
<td>$5 \times 10^{-2}$</td>
<td>600</td>
<td>9.8</td>
<td>No Ni</td>
</tr>
<tr>
<td>Cu(NO$_3$)$_2$</td>
<td>3%</td>
<td>Ni#9</td>
<td>$2 \times 10^{-2}$</td>
<td>1440</td>
<td>9.8</td>
<td>No Ni</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni#10</td>
<td>$3 \times 10^{-2}$</td>
<td>1440</td>
<td>10.0</td>
<td>No Ni</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni#11</td>
<td>$4 \times 10^{-2}$</td>
<td>1440</td>
<td>10.1</td>
<td>No Ni</td>
</tr>
</tbody>
</table>

The use of Ag as the nucleating agent did not result in Ni reduction. The bilayer phase had a light lavender color immediately after the reduction by N$_2$H$_4$. At 55°C, Ni#6 to Ni#8 started changing to a light brown color in 30 minutes and remained the same even after 10 hours. The lack of Ni formation by Ag is consistent with the large disregistry (16%) between Ag and Ni lattices.
With a small amount of Cu as a nucleating agent, the bilayer phase had a light lavender color immediately after the reduction of N₂H₄, which changed to lavender grey in the next 2.5 hours, then remained the same after 1 day. This indicated that the small amount of Cu nuclei generated was not enough to stimulate the Ni formation in the POE-water bilayer template.

The morphology of the Ni primary particles (Ni#5) was examined under AFM and is shown in Figure 7.4. The platelets had a face diameter of 36 ± 5 nm (±95% confidence interval, n = 6), a thickness of 8 ± 1 nm (±95% confidence interval, n = 6), and an aspect ratio of ~4.5.

![X-ray diffraction pattern](image)

Figure 7.3. X-ray diffraction pattern of Ni nanoparticles synthesized in a POE-aqueous bilayer system and reduced by N₂H₄·xH₂O at pH 9.5 and 55 ±1°C (thermal bath), followed by three washing iterations in ethanol. 0.04 M NiCl₂ was used as the Ni source. The Pd/Ni molar ratio was 5 × 10⁻². The pattern was taken with Cu Kα X-rays.
Figure 7.4. AFM images of Ni nanoplatelets synthesized in a POE-aqueous bilayer system and reduced by N$_2$H$_4$·xH$_2$O at pH 9.5 and 55 ±1°C (thermal bath). 0.04 M NiCl$_2$ was used as the Ni source. $5 \times 10^{-2}$ molar ratio of Pd/Ni was used as the nucleating agent. The platelets have a face diameter of 36 ± 5 nm (± 95% confidence interval, n = 6), a thickness of 8 ± 1 nm (± 95% confidence interval, n = 6), and an aspect ratio of ~ 4.5.
7.3.2 Reduction of Cu/Ni Nanoplatelets

For the potential application of a Cu/Ni alloy in MLCC, the Cu/Ni ratio was determined based on the eutectic temperature of the Ag70/Pd30 electrode (~1200°C). The Ag/Pd alloys have been widely used as internal electrodes in the MLCC industry. For BaTiO₃-based dielectrics sintered at 1100 °C, Ag70/Pd30 is usually used as the internal electrode. The Cu-Ni binary phase diagram shows that to obtain the same eutectic temperature, the atomic ratio of Cu/Ni must be very close to Cu₀.₈₁/Ni₀.₁₉. Therefore, the preliminary Cu/Ni nanoplatelet synthesis was focused on the composition of Cu₈₁/Ni₁₉ in the POE-water system.

0.04 M Cu(NO₃)₂ and 0.04 M NiCl₂ were mixed at a molar ratio of 81:19 to be used as a precursor for the Cu/Ni synthesis. The total [water]/[POE] molar ratio was kept at 13.4. The color changes after reduction are listed in Table 7.4. When Cu(CH₃CO₂)₂ was used as the Cu source, after being reduced by N₂H₂·xH₂O and kept for 4 hours in equilibrium at 55°C, the color of the bilayer gradually changed from indigo to black, indicating a possible Ni reduction. The synthesized powder remained black after being washed four times in a pH-adjusted ethanol. However, the dry powder changed to a dark green color after being kept in air for 1 day. XRD analysis indicated that the dark green powder is a mixture of two phases, the major phase being Cu₂O, and the secondary phase being Cu₀.₈₁Ni₀.₁₉. With the use of CuCl₂ as the Cu source, the synthesized powder was unstable in air, and changed its color to a greenish yellow in 1 day. Cu₀.₈₁Ni₀.₁₉ synthesized by using Cu(NO₃)₂ is stable in air. Energy-dispersive spectroscopy (EDS) verified that the atomic ratio of Cu/Ni is 81:19, as shown in Figure 7.5. XRD analysis
shows that the major phase is Cu$_{0.81}$Ni$_{0.19}$ with a secondary phase of Cu$_2$O (Figure 7.6). The weight composition of each phase was quantitatively calculated using the reference intensity ratio (RIR) method described earlier in Chapter 2. It was determined that the compositions of Cu$_{0.81}$Ni$_{0.19}$ and Cu$_2$O were 80 wt% and 20 wt% in the mixed compound.

Table 7.4. Color change observations in the reduction of Cu/Ni powders. The concentration of the Cu precursor is 0.04 M.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu Precursor</th>
<th>Synthesis condition</th>
<th>Dry powder color change</th>
</tr>
</thead>
<tbody>
<tr>
<td>#YY440b</td>
<td>Cu(CH$_3$CO$_2$)$_2$</td>
<td>55°C/4hrs, pH 8.9</td>
<td>Black $\rightarrow$ deep green in 1 day</td>
</tr>
<tr>
<td>#YY445a</td>
<td>CuCl$_2$</td>
<td>55°C/4hrs, pH 8.9</td>
<td>Black $\rightarrow$ greenish yellow in 1 day</td>
</tr>
<tr>
<td>#YY440a</td>
<td>Cu(NO$_3$)$_2$</td>
<td>55°C/4hrs, pH 8.9</td>
<td>Remains black</td>
</tr>
</tbody>
</table>

Figure 7.5. Elemental analysis by energy-dispersive spectroscopy (EDS) verifies that the atomic ratio of Cu/Ni is 81:19 using Cu(NO$_3$)$_2$ as copper nucleating agent (#YY440a). The elemental analyses were performed four times on different surface regions. #YY440a contains 75.07 ± 2.20 atomic% Cu and 18.54 ± 1.78 atomic% Ni, which gives a atomic ratio of 81:19 after being normalized. There is 3.17 ± 0.12 atomic% of Cl present in the as synthesized powder, which might result from the NiCl$_2$ precursor and was not removed completely from washing. EDS courtesy of Gregory Hayes.
Figure 7.6. X-ray diffraction pattern of Cu/Ni nanoparticles synthesized in POE-aqueous bilayer system and reduced by N$_2$H$_4$·xH$_2$O at pH 9.5 and 55 ±1°C (thermal bath), followed by three washing iterations in ethanol. 0.04 M Cu(NO$_3$)$_2$ and 0.04 M NiCl$_2$ were mixed at a molar ratio of 81:19 as the precursor for the Cu/Ni synthesis. The pattern was taken with Cu Kα X-rays.
The morphology of the Cu_{0.81}/Ni_{0.19} primary particles was examined under AFM, shown in Figure 7.7. The platelets had a face diameter of 180 ± 5 nm (± 95% confidence interval, n = 5), a thickness of 9 ± 1 nm (± 95% confidence interval, n = 5), and an aspect ratio of ~ 20. Based on the Cu_{0.81}/Ni_{0.19} platelet morphology, a monolayer of Cu_2O with a thickness of 0.426 nm on the surface of a Cu_{0.81}/Ni_{0.19} nanoplatelet is a ~ 7 wt%. A layer of Cu_2O with a thickness of 1.2 nm on the surface of a Cu_{0.81}/Ni_{0.19} nanoplatelet gives ~ 20 wt%. The Cu_2O phase on the surface of Cu_{0.81}/Ni_{0.19} might come from the drying of as-synthesized Cu_{0.81}/Ni_{0.19} in air.

The hot-stage XRD analysis of Cu_{0.81}/Ni_{0.19} in ultra high purity N_2 also shows that Cu_{0.81}/Ni_{0.19} nanoplatelets are sensitive to the O_2 content in the atmosphere. Hot stage XRD analysis was performed on the synthesized Cu_{0.81}/Ni_{0.19} platelet powders (#YY440a) in high purity N_2 (oxygen content less than 2 ppm). The results indicated that the Cu_{0.81}/Ni_{0.19} alloy powder is sensitive to the small oxygen content in the atmosphere. As shown in Figure 7.8, the composition of Cu_2O increased with the consumption of the Cu_{0.81}/Ni_{0.19} phase at elevated temperatures, from 20 wt% at room temperature to 38 wt%, and to 65 wt% at 200 ºC and 300 ºC. The weight percent was determined by using quantitative analysis with the reference intensity ratio (RIR) method. In addition, CuO formed at 500 ºC in ultra high purity N_2 that contained 80 wt% of total weight of CuO and Cu_{0.81}/Ni_{0.19} mixture. Cu_{0.81}Ni_{0.19} nanoplatelets were more sensitive to the oxygen content in the atmosphere than Ni nanoplatelets synthesized using a similar synthetic method (see Appendix F). Therefore, much care must be taken to avoid oxidation by any oxygen contamination during synthesis and processing.
Figure 7.7. AFM images of Cu$_{0.81}$/Ni$_{0.19}$ nanoplatelets synthesized in a POE-aqueous bilayer system and reduced by N$_2$H$_4$ ·xH$_2$O at 55 ±1°C (thermal bath). The platelets have a face diameter of 180 ± 5 nm (± 95% confidence interval, n = 5), a thickness of 9 ± 1 nm (± 95% confidence interval, n = 5), and an aspect ratio of ~ 20.
Figure 7.8. Hot stage X-ray diffraction pattern of Cu_{0.81}/Ni_{0.19} nanoparticles in an ultra high purity nitrogen atmosphere (oxygen content is less than 2 ppm). The Cu_{0.81}/Ni_{0.19} reduction was carried out in a POE-water bilayer system by hydrazine hydrate at 55°C for 4 hours. The Cu_{0.81}/Ni_{0.19} nanoparticles were oxidized to CuO without any formation of nickel hydride compound.
Hot stage XRD analysis was performed under a vacuum (10^{-5} \text{ bar}) with the Cu_{0.81}Ni_{0.19} as synthesized powder, as shown in Figure 7.9. No further copper oxidation was observed for temperatures below 500°C. The Cu_{0.81}Ni_{0.19} peak for (111) direction increased with increasing temperature.

Figure 7.9. Hot stage X-ray diffraction pattern of Cu_{0.81}/Ni_{0.19} nanoparticles under vacuum (10^{-5} \text{ bar}). The Cu_{0.81}/Ni_{0.19} reduction was performed in a POE-water bilayer system by hydrazine hydrate at 55°C for 4 hours. The crystallite size increased with increasing temperature.
becomes more narrow with the increase in temperature implying that the crystallite size increases with the temperature. Unfortunately, quantitative crystallite size can not be accurately calculated by the Scherrer equation, because the heterogeneous nucleation introduced a significant amount of strain in the platelet formation. Therefore the Scherrer equation (Eq. 2.6) is not applicable. Hall Williamson method was used to determine the crystallite size and the amount of strain associated with the increase of temperature. It was shown that at temperature below 500°C, the diffraction at (220) were too weak to perform accurate estimation. At 500°C, Cu₀.₈₁/Ni₀.₁₉ appeared to be more crystalline, and the crystallite size estimated was ~ 370 nm with a 0.142 % strain associated.

7.4 Conclusions

Ni nanoplatelets and Cu₀.₈₁/Ni₀.₁₉ nanoplatelets were prepared in a POE-water bilayer system. The nucleation of Ni was stimulated by the introduction of Pd(NO₃)₂ solution with a Pd/Ni molar ratio of 5×10⁻². The synthesized Ni nanoplatelets had an average face diameter of 36 ± 5 nm and an average thickness of 8 ± 1 nm (± 95% confidence interval, n = 5). It was shown that base metal Cu₀.₈₁Ni₀.₁₉ with average face diameter of 180 ± 5 nm and an average thickness of 9 ± 1 nm (± 95% confidence interval, n = 5) synthesized through a POE-water bilayer system. Cu₀.₈₁Ni₀.₁₉ nanoplatelets were more sensitive to the oxygen content in the atmosphere than Ni nanoplatelets synthesized through the same method (see Appendix F). Therefore, much care must be taken to avoid oxidation by any oxygen contamination during synthesis and processing.
7.5 References


Chapter 8

Conclusions and Suggested Work

8.1 Summary and Conclusions

In addition to controlling morphology during synthesis, the current study investigated the synthesis of Ag, Cu, Ni and Cu/Ni nano-alloy in a polyoxyethylene (POE)-water bilayer phase. For large-scale fabrication, higher yields of Ag nanoplatelets (20 g/liter) and Cu nanoplatelets (12 g/liter) are achieved in a POE-water bilayer system. Metal precursors (i.e. AgNO₃ and Cu(NO₃)₂) in higher concentrations are used to obtain a higher yield synthesis of metal nanoplatelets and raised some critical concerns about the presence of a lamellar phase in the POE-water binary phase diagram. With the increase in [NO₃]⁻ concentration, the oxyethylene-water interaction decreases due to the dehydration of the POE head group. Phase separation is induced when the ion concentration reached the upper limit of the current investigation at 1 M. Therefore, the [water]/[surfactant] molar ratio has to be decreased to compensate for the dehydration of the POE head groups and maintain the bilayer phase structure. For the higher yield Cu nanoplatelet synthesis, an elevated temperature is required to increase the reaction rate. The free energy ($\Delta G_f$) of the oxyethylene(EO)/water structure is expected to be proportional to the number of EO units.¹ As the temperature increases, the $\Delta G_f$ decreases, which results in a favorable EO/EO interaction instead of an EO/water
interaction. When the temperature reaches the upper limit, phase separation occurs due to the dehydration of water as EO/water interactions become less favorable.

Laundering nanoparticles after synthesis and recovering them in a well-dispersed state is another focus of the current work. A protection-dispersion approach has been developed to stabilize the Ag nanoplatelets in ethanol. Polyethylenimine (PEI) is used to form a protective polymer layer with a low charge in initial washing iterations, to promote reversible flocculation. The solution pH is then adjusted to provide a charge in the final wash, promoting electrosteric dispersion. A PEI adsorption isotherm is established to quantitatively estimate the adsorption density. A passivation-dispersion approach is used to stabilize the high yield Cu nanoplatelets in an ethanol-water (7:3, vol%) co-solvent. In this approach, a complexing agent is applied to the particle surface to form a stable complex with the metal ions over a wide range of pH and provide a surface charge to promote dispersion in the suspension. Oxalic acid (HOx) and citric acid (HCit) are investigated as the passivation-dispersion agents. HCit is shown to successfully stabilize the Cu nanoplatelets in a $10^{-3}$ M concentration with respect to the solid loading. It is also shown that citrate on the surface of the Cu nanoplatelets provides a zeta potential of the order of -25 mV, which is sufficient to provide dispersion. Sedimentation experiments and an electrostatic deposition technique reveal that with the use of citric acid, well-dispersed Cu nanoplatelet suspensions are obtained at above pH 8.

Ni nanoplatelets were synthesized in POE-water bilayer system. To maintain POE-water self-assembled lamellar structure, synthesis temperature needs to be controlled below ~60°C. With the temperature constrain, synthesis of pure phase Ni was conducted by the application of Pd at a molar ratio of $5\times10^{-2}$ Pd/Ni. Cu$_{0.81}$/Ni$_{0.19}$
bimetallic nanoplatelets have also been synthesized in the same system using Cu as the nucleating agent. The atomic ratio was verified by energy-dispersive spectroscopy.

A novel approach has also been developed for the first time to statistically evaluate the morphology of the tabular shape nanoparticles using AFM analysis based on a relatively large population (n>200). The novel approach uses color delineation in the 3rd dimension (i.e., thickness) to produce both thickness and face diameter in the semi-automated analysis of several hundred nanoplatelets to quantify physical dimensions as well as to assess the degree of dispersion.

8.2 Suggested Work

In the current work, silver (Ag), copper (Cu), nickel (Ni) and copper/nickel (Cu$_{0.81}$/Ni$_{0.19}$) nanoplatelets are synthesized in a self-assembled polyoxyethylene-water bilayer system. However, the oxidation properties of Ag and Ni nanoparticles should be studied in more detail by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The syntheses of Ni nanoplatelets and Cu$_{0.81}$/Ni$_{0.19}$ alloy are studied in the current work. As has developed for Ag and Cu nanoplatelets, the higher yield synthesis of Ni nanoplatelets and phase pure Cu$_{0.81}$/Ni$_{0.19}$ alloy synthesis are worth pursuing in the future.

The compaction of randomly orientated copper nanoplatelets was studied under a vacuum (see Appendix C). A large spring back phenomena is observed which prevents the Cu pallet from maintaining a high green density at room temperature. The green density of the Cu pallet drops ~ 35 % at room temperature. Warm compaction of Cu
nanoplatelets is conducted at 200 °C under vacuum to minimize the spring back effect. At 200°C, the green density of the Cu pallet dropped ~ 10 % due to spring back effect. To eliminate the spring back effect, it is proposed that Cu nanoplatelets should be orientated and laminated before the compaction.

Electrostatic layer-by-layer deposition exploits Coulombic interactions among oppositely-charged surfaces, whether molecular or condensed matter, that are adsorbed from dilute solutions in alternating layers. It has also been shown that this approach can be used to build ordered multilayer films (hundreds of layers) with various combinations of particulates, molecular fragments, inorganic and organic layers, biomolecules, photochromic molecules, and conductive polymers. Therefore, metal films can be deposited using well-dispersed Ag nanoplatelets and Cu nanoplatelets by electrostatic deposition. The film thickness and the electrical properties should be measured as a function of solid loading and the deposition time.

Electrophoretic deposition (EPD) is proposed as another technique for the deposition of thin metal films in passive electronic components. Well-dispersed Ag nanoplatelets in ethanol can be formed by EPD. Traditional EPD is limited in organic solvent to limit the formation of hydrogen bubbles at the cathode during deposition. Uchikoshi et al. recently reported the potential to deposit alumina and titania in an aqueous solution using an applied voltage of 30 V with Pd electrodes. Pd electrodes have been found to be able to form PdHx with hydrogen and adsorb hydrogen generated at the cathode to stop the formation of hydrogen bubbles. Therefore, Cu nanoplatelet dispersion in an ethanol-water (7:3, vol%) co-solvent can be deposited using Pd electrode by EPD.
8.3 References


Appendix A

Parameter Values Obtained from the Curve Fitting of the PEI Adsorption Isotherm Experimental Data to a Sigmoidal Function

Sigmoidal function used in the curve fitting is given by Eq. (A.1)

\[ \Gamma = \frac{\Gamma_{\text{max}}}{1 + b e^{-kC}} \]  

\[ (A.1) \]

<table>
<thead>
<tr>
<th>Curve (indicated by pH value)</th>
<th>Parameters</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6.5</td>
<td>( \Gamma_{\text{max}} )</td>
<td>0.906</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>55.644</td>
<td>12.093</td>
</tr>
<tr>
<td></td>
<td>k</td>
<td>32.375</td>
<td>2.070</td>
</tr>
<tr>
<td></td>
<td>( \chi^2 )</td>
<td>0.00026</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( r^2 )</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>pH 7.0</td>
<td>( \Gamma_{\text{max}} )</td>
<td>1.148</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>52.390</td>
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<td></td>
<td>k</td>
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<td>( \chi^2 )</td>
<td>0.00018</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( r^2 )</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>pH 7.5</td>
<td>( \Gamma_{\text{max}} )</td>
<td>1.114</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>41.703</td>
<td>14.497</td>
</tr>
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<td></td>
<td>k</td>
<td>33.139</td>
<td>3.730</td>
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<td></td>
<td>( \chi^2 )</td>
<td>0.00103</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( r^2 )</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>pH 8.0</td>
<td>( \Gamma_{\text{max}} )</td>
<td>0.818</td>
<td>0.039</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>47.158</td>
<td>44.681</td>
</tr>
<tr>
<td></td>
<td>k</td>
<td>35.830</td>
<td>10.497</td>
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<tr>
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<td>( \chi^2 )</td>
<td>0.00277</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( r^2 )</td>
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<td></td>
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<tr>
<td>pH 8.5</td>
<td>$\Gamma_{\text{max}}$</td>
<td>b</td>
<td>k</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------</td>
<td>------</td>
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<tr>
<td></td>
<td>0.468</td>
<td>70.074</td>
<td>45.049</td>
</tr>
</tbody>
</table>

Note: $\Gamma$ is the adsorption density of polyethylenimine (PEI) on the surface of Ag nanoplatelets as a function of PEI equilibrium concentration; $\Gamma_{\text{max}}$ is the maximum adsorption density of PEI on the surface of Ag nanoplatelets as a function of PEI equilibrium concentration; $C$ is the PEI adsorption equilibrium concentration; $b$ and $k$ are constants. Levenberg-Marquardt non-liner curve fitting had a tolerance of 0.05.

Reference

Appendix B

STABIL Calculation for Total Interaction Energy

The well-known theory of colloid stability was articulated by Derjaguin-Landau-Verwey-Overbeek (DLVO) in the 1940's. DLVO theory deals with the attraction potential energy resulting from van der Waals attraction between particles and the repulsion potential energy due to electrostatic interaction between like-charged particle surface. The superposition of these two interactions gives the total interaction from which predictions can be made on the stability of a suspension. The computer program STABIL® takes DLVO theory one step further by calculating interaction energy curves for systems where a polymer layer is present on the particles.

Table B.1 is a list of the physical constants used in the calculation of the interaction energy of Ag nanoplatelets with the present of PEI in ethanol solution in Chapter 4.

Table B.1. List of physical constants used in the calculation of the interaction between Ag nanoplatelets with the present of PEI in pure ethanol.

| Hamaker constant of Ag$^{4,5}$ | $A_{11} = 16.4 \times 10^{-20}$ J  
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamaker constant of ethanol$^6$</td>
<td>$4.2 \times 10^{-20}$ J</td>
</tr>
<tr>
<td>Lattice constant of Ag</td>
<td>4.0862 Å</td>
</tr>
<tr>
<td>Face diameter of Ag nanoplatelets</td>
<td>55 nm</td>
</tr>
<tr>
<td>Thickness of Ag nanoplatelets</td>
<td>7 nm</td>
</tr>
<tr>
<td>Ag particle surface area</td>
<td>5961 nm$^2$</td>
</tr>
<tr>
<td>Polymer (PEI) thickness on Ag$^7$</td>
<td>2.8 nm</td>
</tr>
</tbody>
</table>
Table **B.2** is a list of physical constants used in the calculation of the interaction energy of Cu nanoplatelets dispersed in oxalic acid and citric acid in ethanol–water (7:3, vol%) co-solvent in Chapter 6.

Table **B.2.** List of physical constants used in the calculation of the interaction energy of Cu nanoplatelets dispersed in oxalic acid and citric acid in ethanol–water (7:3, vol%) co-solvent.

<table>
<thead>
<tr>
<th>Physical Constant</th>
<th>Value</th>
</tr>
</thead>
</table>
| Hamaker constant of Cu$^{4,5}$ | $A_{11} = 28.4 \times 10^{-20} \text{J}$  
                           | $A_{131} = 17.5 \times 10^{-20} \text{J}$  |
| Lattice constant of Cu | 3.6150 Å                       |
| Face diameter of Cu nanoplatelets | 43 nm                      |
| Thickness of Cu nanoplatelets | 6 nm                          |
| Cu particle surface area | 3715 nm$^2$                   |
| Thickness of a layer of citric acid$^8$ | 1.4 nm                      |
| Thickness of a layer of oxalic acid$^8$ | 0.74 nm                     |

The ionic strength ($I$) of the solvent and the Debye-Hückel parameter ($\kappa$) are calculated from the physical constants and user defined values, given by Eq. (B.1)$^3$ and Eq. (B.2)$^3$

$$I = \frac{\sum_{i=1}^{m} c_i z_i^2}{2} \quad \text{(B.1)}$$

where $m$ is the number of ionic species, $c_i$ is the concentration (mol/L) of $i$th species, and $z_i$ is the valence of $i$th species.

$$\kappa = \sqrt{\frac{8\pi e^2 I}{1000 N_A \epsilon_0 k_d k_B T}} \quad \text{(B.2)}$$
where $e$ is the charge on electron ($1.602 \times 10^{-19}$ C), $N_A$ is the Avogadro's number (6.023 $10^{23}$ ions/mol), $\varepsilon_o$ is the dielectric permittivity of a vacuum ($1.11265 \times 10^{-10}$ F/m), $k_d$ is the relative dielectric constant, $T$ is the absolute temperature (K) and $k_B$ is the Boltzmann's constant ($1.38054 \times 10^{-23}$ J/K).

The separation distance between two overlapping double layers is given by integrating the Poisson-Boltzmann equation twice, Eq. (B.3)$^3$

$$D = \frac{\int_{\psi_d}^{\psi_d/2} 2d\psi(x)}{\int_{\psi_d/2}^{\psi_d} \sqrt{\frac{8\pi k_B T}{\varepsilon_o k_d}} \sum_{i=1}^{m} n_i \left[ \exp\left(-\frac{z_i e \psi(x)}{k_B T}\right) - \exp\left(-\frac{z_i e \psi_d/2}{k_B T}\right) \right]}$$

(B.3)

where $\psi(x)$ is the potential at distance $x$ from the particle, and $\psi_d/2$ is the potential at the “midpoint” of two interacting Stern planes. Using the flat-plate model, when a layer of adsorbed ions is present on a surface, the total repulsive energy is given by Eq. (B.4)$^3$

$$V_{R-\text{pl}}(D) = 2[V(D) - V_{\infty}]$$

(B.4)

where $V(D)$ and $V_{\infty}$ are given by Eq. (B.5)$^3$ and Eq. (B.6)$^3$

$$V(D) = -\frac{k_B T D}{2} \sum_{i=1}^{m} n_i \left[ \exp\left(-\frac{z_i e \psi_d/2}{k_B T}\right) - 1 \right] + \sqrt{\frac{\varepsilon_o k_d k_B T}{2\pi}} \int_{\psi_d/2}^{\psi_d} \sqrt{\sum_{i=1}^{m} n_i \left[ \exp\left(-\frac{z_i e \psi(x)}{k_B T}\right) - \exp\left(-\frac{z_i e \psi_d/2}{k_B T}\right) \right]} d\psi(x)$$

(B.5)

$$V_{\infty} = \sqrt{\frac{\varepsilon_o k_d k_B T}{2\pi}} \int_{0}^{\psi_d/2} \sqrt{\sum_{i=1}^{m} n_i \left[ \exp\left(-\frac{z_i e \psi(x)}{k_B T}\right) - 1 \right]} d\psi(x)$$

(B.6)

The attractive van der Waals interaction is calculated by Eq. (B.7)$^3$
where $A_{131}$ is the Hamaker constant of particle 1 in a medium 3. The total interaction energy of the particle is the summation of the attractive and repulsive energies, given by Eq. (B.8)

$$V_{T_{pl}}(D) = V_{R_{pl}}(D) + V_{A_{pl}}(D)$$  \hspace{1cm} (B.8)

Figure B.1 is a series of interaction energy curves calculated using STABIL for the Ag nanoplatelets with the present of PEI. Figure B.2 is a series of interaction energy curves calculated using STABIL for the Cu nanoplatelets and Cu nanoplatelets dispersed in $10^{-2}$ M oxalic acid (HOx) and $10^{-3}$ M citric acid (HCit)
Figure B.1. Total interaction energy curves for the Ag nanoplatelets with the present of PEI at various PEI concentrations in ethanol solution. The curves were calculated by STABIL using flat plate modal and the physical constant in Table B.1.
Figure B.2. A series of interaction energy curves calculated using STABIL for the Cu nanoplatelets in ethanol-water (7:3, vol%) and Cu nanoplatelets dispersed in $10^{-2}$ M oxalic acid (HOx) and $10^{-3}$ M citric acid (HCit). The curves were calculated by STABIL using flat plate model and the physical constant in Table B.2.

References


Appendix C

Compaction of Randomly-Oriented Copper Nanoplatelets

The compaction of higher yield (12g/liter) Cu nanoparticles was performed at 25°C and 200°C using a Carver press (Model #3912, Carver Inc. Wabash, USA). The density change as a function of pressure was measured. The microstructure of the as-pressed Cu pellet was examined with a field emission scanning electron microscope (FE-SEM, JEOL 6700F, Japan).

The uniaxial compaction of metal powders is widely used to produce net- or near-net-shaped components and to consolidate materials that are subjected to further mechanical work.¹ The process typically consists of die filling with homogeneous powders, pressing to a desired pressure, releasing the pressure and ejecting the compact from the die. The compaction of randomly oriented Cu nanoplatelets was performed at room temperature (25°C, cold pressing) and elevated temperature (200°C, warm pressing). The goal in particle compaction is to achieve an increased density by applying an external pressure. The important processes in cold compaction consist of powder rearrangement and reorientation, elastic deformation, plastic deformation and bulk compression.² The compaction behavior of tabular Cu nanoparticles was plotted as a function of applied pressure at room temperature and at 200°C under a vacuum. Figure C.1 The apparent density of the Cu compaction was ~ 23% theoretical density (TD) at 25°C, where the particles had a low number of particle contacts. Rearrangement
occurred at a pressure less than ~0.05 MPa. At this stage, the particles started with a packing density characteristic of random packing.

Figure C.1. Compaction diagram of Cu nanoplatelets at room temperature and 200 °C under a vacuum. The Cu nanoplatelets were synthesized in a POE-water bilayer system. Due to the spring back effect, the final green density of the Cu pallet at room temperature dropped to ~ 55 % T.D., and the final green density of the Cu pallet at 200 °C dropped to ~ 80 % T.D. The inserted picture of a Cu pallet was compressed at room temperature at 350 MPa.
Irregular particles undergo considerable rearrangement at a low compaction pressure, and the rearrangement contribution to densification is nontrivial. The random orientation of the Cu nanoplatelets was the main cause of low densification. Particle rearrangement and flow ability were limited by the tabular nature of the morphology. Following the rearrangement, localized deformation was appeared from ~1 MPa to ~150 MPa, accompanied by an increased density from 35% T. D. to 60%. T. D. The increased pressure enlarged the contacts and provided closer packing with a lower porosity and smaller pores. Localized plastic deformation occurred at the contact points between particles. The coordination number increased as the load was distributed over more particles. When the pressure was increased from 150 MPa, the localized deformation led to a homogenous deformation throughout the compact and the green density was increased to a ~90% theoretical density at 350MPa. In this third stage, the deformation was throughout the particle mass. Particles able to undergo plastic deformation become strain hardened, increasing their resistance to further deformation. That is, the combination of an increased coordination number, the increased particle resistance to deformation and the enlarged contact areas acted together to resist further deformation. No bulk compression was observed for the compaction of Cu nanoplatelets at room temperature, in which the plastic deformation was exhausted and the compact was nearly fully dense. When ejected from the die, the spring back effect associated with a large elastic relaxation was observed for Cu tabular particles. At room temperature a withdrawal of ~35 % T. D. was associated with the elastic relaxation for the Cu nanoplatelets. The microstructure of the pellet ejected from the die after the complete
compression is shown in Figure C.2. It was seen that most of the Cu platelets were deformed in order to form close contacts.

In order to minimize the spring back effect, elevated temperature compaction was carried out at 200°C under vacuum. Warm compaction is effective due to thermal softening. At 200°C, the apparent density was ~ 32% T. D. higher than that at room temperature. The slight softening of the powder contributed to the density gain. Initial densification was by particle rearrangement and plastic flow at the particle contacts below ~150 MPa, with a change in fractional density from 32% to 58% T. D.. Above 150 MPa, the fractional density increased steeply from 58% to 90% T. D.. The increased pressure overcame the yield strength and powders were deformed to release the stress. The densification was due to the creep and volume diffusion of copper under the high pressure. In warm compaction, a lower pressure (~275 MPa) was applied to achieve a 90% theoretical density while the same densification was achieved under a pressure of ~350 MPa for cold compaction. There was still a ~ 10% density decrease associated with elastic relaxation. The green compaction density of the Cu was limited to ~ 80 % on account of the spring back effect after the pellet was ejected from the die. The tabular shape was the main factor inhibiting the higher green density.
Figure C.2. (A) SEM image of the natural surface of the Cu pellet after being compressed at 350 MPa at room temperature. (B) SEM image of the same sample at a higher magnification. The Cu nanoplatelets were synthesized in a POE-water bilayer system with a theoretical yield of 12 g/liter.
References


Appendix D

The Richardson-Ellingham Diagram for Cu₂O and CuO

Oxidation reactions of Cu are given by Eq. (D.1) and Eq. (D.2)

\[
4\text{Cu} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{O} \quad (\text{D.1})
\]

\[
2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO} \quad (\text{D.2})
\]

The Gibbs free energy change \((\Delta G^\circ_T)\) at a temperature \(T\) can be calculated from values of \(\Delta H^\circ_T\) and \(\Delta S^\circ_T\) as follows Eq. (D.3)

\[
\Delta G^\circ_T = \Delta H^\circ_T - T\Delta S^\circ_T \quad (\text{D.3})
\]

For copper oxidation reactions, equilibrium oxygen pressure is a function of temperature, and the relationship among the variables is given by Eq. (D.4)

\[
\Delta G^\circ = RT \ln P_{\text{O}_2} \quad (\text{D.4})
\]

Table D.1 is a list of the thermodynamic properties used in the calculation of the Gibbs free energy.

Table D.1. Thermodynamic properties of formation of inorganic substances²

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>(\Delta H^\circ_{f(298.15)}) kcal/mole</th>
<th>(\Delta G^\circ_{f(298.15)}) kcal/mole</th>
<th>(S^\circ_{f(298.15)}) cal/(mole·degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0</td>
<td>0</td>
<td>7.97 ± 0.02</td>
</tr>
<tr>
<td>O₂</td>
<td>0</td>
<td>0</td>
<td>49.003 ± 0.008</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>-40.83 ± 0.3</td>
<td>-35.36</td>
<td>22.08 ± 0.1</td>
</tr>
<tr>
<td>CuO</td>
<td>-37.23 ± 0.15</td>
<td>-30.59</td>
<td>10.19 ± 0.05</td>
</tr>
</tbody>
</table>
Figure D.1. \( \Delta G^\circ \) as a function of temperature for oxides of copper, showing regions of stability for Cu, Cu\(_2\)O and CuO

References

Appendix E

Estimation for Average Number of Edge: Side Surface: Top Surface: Bulk of Cu Nanoplatelet

Higher yield Cu nanoplatelet (12 g/l)

Constant: \( \rho = 8.96 \text{ g/cm}^3, M = 63.55 \text{ g/mol}, N_0 = 6.02 \times 10^{23} \text{ atoms/mol} \)

Cu platelet average dimension: \( d = 43 \text{ nm}, t = 6 \text{ nm} \) (high yield Cu)

\[ \frac{\rho}{M} N_0 = \frac{8.96}{63.55} \times 6.02 \times 10^{23} = 8.5 \times 10^{22} \text{ (atoms/cm}^3) = 85 \text{ (atoms/nm}^3) \]

(2) Number of atoms in one single Cu platelet:

The volume of one single Cu platelet is: \( V_{Cu} = \pi \times (d/2)^2 \times t = 8713 \text{ (nm}^3) \)

Total number of atoms in one Cu platelet \( N_{total} = 8713 \times 85 = 740,605 \text{ (atoms)} \)

(3) Dimension of each Cu atom:

\( a = 3.615\text{Å} = 0.3615 \text{ nm} \)

\( A = a^2 = (0.3615)^2 = 0.1307 \text{ nm}^2 \)

(4) Number of atoms at the edge
\[ L_{\text{edge}} = \pi d = 135 \text{ nm} \]

Number of atoms at each edge = \[ \frac{L_{\text{edge}}}{a} = 135/0.3615 = 373 \text{ (atoms)} \]

Considering 2 edges, the total number of atoms: \[ N_{\text{edge}} = 373 \times 2 = 747 \]

(5) Number of atoms at the side surface

Area of the side surface: \[ A_{\text{side}} = \pi \times d \times (t-2a) = 713 \text{ nm}^2 \]

Number of atoms at the side surface: \[ N_{\text{side}} = \frac{A_{\text{side}}}{A} = 713/0.1307 = 5,455 \]

(6) Number of atoms at the top surface

Area of the top surface: \[ A_{\text{top}} = \pi \times \left( \frac{d}{2} - a \right)^2 = 1404 \text{ nm}^2 \]

Number of atoms at each top surface = \[ \frac{A_{\text{top}}}{A} = 1404/0.1307 = 10740 \text{ (atoms)} \]

Total number of atoms at the top surface: \[ N_{\text{top}} = 10740 \times 2 = 21,480 \]

(7) Number of atoms in the bulk

\[ N_{\text{bulk}} = N_{\text{total}} - N_{\text{edge}} - N_{\text{top}} - N_{\text{side}} = 740605 - 747 - 21480 - 5455 = 712,923 \]

(8) Atom number ratio of edge: side surface: top surface: bulk

Appendix F

Hot Stage XRD Analysis of Incomplete Ni reduction using Pd as Nucleating Agent

As described in Chapter 7, a brief summary of the Ni reduction results is listed in Table F.1. The reduction of samples (Ni#1 to Ni#4) remained a light grey color after being held at 55ºC for 120 minutes, and XRD analysis showed incomplete reduction to Ni, as shown by the Figure F.1. The reduction of Ni, using $2 \times 10^{-2}$ and $1 \times 10^{-2}$ molar ratios of Pd/Ni resulted in a Ni phase and unknown phases which were not identified. TEM of the incomplete reduction of Ni synthesis (Ni#2) gave a dendritic structure covering the surface of the Ni particles, as shown in Figure F.2. Most of the “nano-thorns” on the particles have a length of 100 nm, which might result from the crystallite phases that could not be identified by XRD analysis at a $2\theta < 40^\circ$. Energy-dispersive spectroscopy (EDS) on the “nano-thorns” structure in Figure F.3 shows that the dendritic structure is a compound of Ni with light elements, such as C, O or H. Carbon and copper peaks in the EDS spectrum may come from the TEM copper grid and lacy carbon film. To further identify the dendritic structure, electron energy-loss spectrometry (EELS) was performed on the dendritic structure. As shown in Figure F.4, $L_{23}$ white lines with a significant shoulder between $L_3-L_2$ indicate the dendritic structure is element Ni instead of NiO. The exist O K-shell may result from free O$_2$ binded on the Ni surface. From the EDS and EELS analyses, the “nano-thorns” structure may be a nickel hydride compound.
Table F.1. Brief summary of experimental conditions for Ni synthesis using Pd(NO₃)₂ as the nucleating agent.

<table>
<thead>
<tr>
<th>Nucleating agent</th>
<th>Disregistry with Ni</th>
<th>Sample ID#</th>
<th>Nucleating agent/Ni molar ratio</th>
<th>Time/mins (55°C)</th>
<th>pH</th>
<th>XRD Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(NO₃)₂ 10%</td>
<td>Ni#1 1 ×10⁻²</td>
<td>120</td>
<td>9.5 Ni &amp; Unknown</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni#2 2 ×10⁻²</td>
<td>120</td>
<td>9.7 Ni &amp; Unknown</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni#3 3 ×10⁻²</td>
<td>120</td>
<td>9.9 Ni &amp; Unknown</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni#4 4 ×10⁻²</td>
<td>120</td>
<td>10.0 Ni &amp; Unknown</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure F.1. X-ray diffraction pattern of Ni nanoparticles synthesized in a POE-aqueous bilayer system and reduced by N₂H₄·xH₂O at pH 9.5 and 55 ±1°C (thermal bath), followed by three washing iterations in ethanol. 0.04 M NiCl₂ was used as the Ni source. The pattern was taken with Cu Kα X-rays. The phases below 2θ < 40° are unknown phases.
Figure F.2. TEM image of incomplete Ni reduction in a POE-water system with the application of Pd as a nucleating catalyst at a $2 \times 10^{-2}$ molar ratio of Pd/Ni. The crystallized dendritic structure on the particle surface may be associated with the unidentified phase in the XRD analysis at $2\theta < 40^\circ$. 
Figure F.3. Energy dispersive spectrum of the “nano-thorn” structure shows that it is a compound of Ni with light elements, such as C, O or H. Cu and C peaks may come from the TEM copper grid and lacy carbon film.
To monitor the possible *in-situ* phase change, hot stage XRD analysis was conducted on the $2 \times 10^{-2}$ Pd/Ni seeded sample in a high purity nitrogen atmosphere. As shown in Figure F.5, nickel hydride (HNi$_2$) began to appear as the temperature increased.

Figure F.4. O K-shell and Ni $L_{23}$ edge spectra from EELS analysis on the dendritic structure. $L_{23}$ white lines with a significant shoulder between $L_3$-$L_2$ indicate the dendritic structure is element Ni instead of NiO. The exist O K-shell indicates that free O$_2$ might bind on the Ni surface.
to 200°C, creating a slightly reducing atmosphere. At 300°C, HNi₂ became the major phase, and at 500°C the sample changed back to the Ni phase. After the sample was cooled to 200°C, the XRD result remained the same as at 500°C.

![XRD pattern](image)

Figure F.5. In an ultra high purity nitrogen atmosphere (oxygen content is less than 2 ppm), the hot stage X-ray diffraction pattern of Ni nanoparticles synthesized by the addition of a 2×10⁻² molar ratio of Pd/Ni. The Ni reduction was carried out in the POE-water bilayer system by hydrazine hydrate at 55°C.
This indicated that during synthesis, fairly concentrated and disordered H-doping of Ni formed as the result of the reduction with hydrazine. In the presence of heat, the H atoms drive the rearrangement of the Ni atoms to a hydride structure. At a higher temperature, the hydrogen was released or rapidly diffused and the Ni structure returned to elemental form (i.e., the hydride was not stable at a high temperature and low H-pressure). In conclusion, the mixed Ni and “nano-thorns” phases had a “self-cleaning” step in the early stages of heating, and Ni may be further reduced in a pure Ni phase in an ultra high purity of N₂ atmosphere with O₂ content less than 2ppm at 500°C.

References

VITA

Ying Yuan

Ying Yuan was born on March 5, 1975 in Tianjin, the People’s Republic of China. After graduating from Yao-Hua high school in 1993, she joined the Tianjin University, Department of Materials Science and Engineering, where she obtained a B.S. degree in Ceramic Engineering in 1997 and then a M.S. degree in the same major in 2000. From there she worked as a visiting scholar in Brunel University’s Department of Mechanical Engineering until August 2001. In September 2001, she joined the University of Manchester’s Materials Science Center as a graduate student and got her M. Phil. degree in Materials Science. In the summer of 2003, Ying entered the Pennsylvania State University to begin her PhD studies in the Department of Materials Science and Engineering, under the guidance of Dr. James H. Adair.