THE STUDY OF NUCLEATION DYNAMICS OF SILVER NANOPARTICLES

Amit Acharya

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Committee:

Mikhail Zamkov, Advisor

Alexey T. Zayak
The advancement of nanoparticle shapes during the hot-injection synthesis of nanoparticles is largely determined by the reaction restricted rate of monomer nucleation. The presence of an activation barrier for monomer assembly provides experimental means for tuning the morphology of colloidal nanocrystals, accessible through a controlled monomer release during the thermal conversion of precursors. Sadly, the monomer concentration in colloidal reactions is hard to track \textit{in situ}, which darkens the real impact of temperature, monomer solubility, and the ligand density on the likelihood of cluster nucleation. Here, we build up an experimental strategy for monitoring the time-dependent monomer concentration during the hot-injection synthesis of Ag nanocrystals. Gold nanoparticles of nearly 5 nm size were synthesized and silver shell was grown over gold under different conditions. The choice of using gold and silver nanoparticles in this experiment lies on the fact that these two nanoparticles have very similar lattices while their Plasmon absorbance peaks are at different wavelengths. This present methodology utilizes Au nanoparticles as chemical probes of the Ag monomer build-up in the reaction flask. The precipitation of Ag on the surface of Au nanoparticles is diffusion–limited and results in a blue-shift of the plasmon resonance which is used to gauge the Ag monomer concentration. By measuring the relative monomer concentration promptly before the nucleation burst, we were able to reveal the role of reaction parameters on the rate of nucleation and the resulting nanoparticle morphology. Specifically, we demonstrate that the nucleation rate is independent of the reaction temperature but is sensitive to the concentration of free ligands in solution.
To my Family
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CHAPTER I. INTRODUCTION

Nanomaterials structure ranges in between those of atoms and bulk materials. They have their dimensions in the nanometer range. Their behavior are determined by their size dependent properties, sensitivity to surface process, and their arrangement in space. Noble metallic nanoparticle show interesting absorbance and scattering properties due to plasmon resonance which occurs when their electron density interact with the incident electromagnetic radiation of wavelength that are far larger than the particle size. Due to these properties, such nanoparticles have been the subject of great interest for the researches around the globe.

Colloidal synthesis of inorganic nanocrystals is a rapidly evolving area of materials science that holds strong promise for future technological applications.\textsuperscript{1-5} Our ability to control the evolution of nanoparticle shapes in colloidal reactions, however, is still evolving. The grand challenge lies in understanding the effect of the reaction parameters, such as precursor concentration, solvent temperature, and ligand chemistry on the progressions of nanocrystal nucleation and growth.\textsuperscript{6-8} Lately, substantial developments in modelling the hot-injection synthesis of inorganic nanocrystals have been attained through revealing the role of the precursor conversion in the product formation.\textsuperscript{9-14} In particular, it was shown that the monomer generation from precursor complexes was the primary reaction-limiting step, which rate can be tuned to control the nanoparticles (NPs) morphology. An enhanced understanding of the colloidal synthesis has allowed reconciling the classical nucleation theory with experimentally observed reaction kinetics\textsuperscript{10} and ensued in the development of new synthetic tactics that enable high nanoparticle yields and narrow size distributions.\textsuperscript{15}
The rate of monomer nucleation during the hot-injection synthesis of colloidal nanocrystals plays an important role in the evolution of nanoparticle shapes. In particular, recent works have shown that the time-dependent monomer concentration, \([M_1(t)]\), represents a key parameter in determining the path of the colloidal reaction.\(^{10}\) Unfortunately, the rate of the monomer build-up during the colloidal growth is difficult to measure experimentally. As a result, the exact effect of the reaction parameters on the process of nanoparticle nucleation, \(nM_1 \rightarrow M_n\), which include solvent temperature, monomer solubility and diffusion, bulk monomer concentration, and the free ligand concentration, is still poorly understood.

Nucleation is basically the initial phase in the progress of either another structure via self-gathering or self-association. Nucleation is commonly considered to be the technique that decides to what extent an observer needs to wait before the new stage or self-sorted out structure shows up. Nucleation in two identical systems can even occur at different times, thus this is a stochastic process.\(^{16-17}\) The impurities present in the system might affect the nucleation process; thus making it necessary to differentiate between the homogeneous and heterogeneous nucleation. Homogeneous nucleation occurs arbitrarily and impulsively without any special nucleation sites within the interior of uniform substance, whereas heterogeneous nucleation occurs at specific nucleation sites like container surfaces, dislodgments, imperfections, and impurities.

According to classical nucleation theory, homogeneous nucleation can be explained on the basis of thermodynamics\(^{18-19}\) by considering the total free energy of a nanoparticle. The total free energy \((\Delta G(r))\) is defined as the sum of surface free energy \((\gamma)\) and the volume free energy \((\Delta G_v)\).\(^{20}\) As a nanoparticle of radius \(r\) is formed in the liquid, the change in Gibbs free energy is

\[
\Delta G(r) = \left(\frac{4\pi}{3}\right) r^3 \Delta G_v + 4\pi r^2 \gamma \quad (1.1)
\]
In Eq.1.1, the value of volume free energy is given by,

$$\Delta G_v = -\frac{K_B T \ln(S)}{V_m},$$  \hfill (1.2)

where \( T = \) temperature, \( K_B = \) Boltzman’s constant, \( V_m = \) molar volume, \( S = \) supersaturation of solution. So, for a particle formation, two factors, \( \Delta G_v \) and \( \gamma \), play significant roles in balancing the total free energy change as shown in figure 1.1. The minimum size of the particle which can survive in the solution without being dissociated, called critical radius \( (r^*) \), can be obtained by setting \( \frac{d\Delta G(r)}{dr} = 0 \), which gives \( r^* = \frac{2\gamma V_m}{K_B T \ln S} \). Also, the nucleation barrier for solidification \( \Delta G^* = \frac{16\pi r^3}{3\Delta G_v^2} \). Further, at \( r = r_0 \), \( \Delta G(r) = 0 \), which implies \( r_0 = -\frac{3\gamma}{\Delta G_v} \).

**Figure**1.1. Free energy diagram explaining Nucleation process in three thermodynamic systems. The plot shows the existence of critical radius \( (r^*) \) and the nucleation barrier \( (\Delta G^*) \).
The free energy diagram shown in figure 1.1 can be explained in three thermodynamic systems. Firstly, the free molecules or atoms form small particles (nucleus) due to nucleation. As the particles grow, $\Delta G(r)$ increases due to the rapid increase of the surface energy, which implies that the particle growth in this phase is not favorable; i.e. most of the particles dissolve back to liquid phase. This is particularly for the case of homogeneous nucleation. Secondly, as the size of particles reach the size of critical radius ($r^*$) and pass the barrier of $\Delta G(r^*)$, further growth of particles will lead to decrease in $\Delta G(r)$, and the particle reaches to the size of $r_0$. So, the number of particles reaching this size would determine the nucleation kinetics of nanoparticles. Thirdly, after passing $r_0$, $\Delta G(r)$ will become more negative, and the growth of particles will be highly favored and eventually lead to the formation of bulk-phase solid as $r$ further increases.

**Figure** 1.2. Barrier energy needed for heterogeneous nucleation is reduced as compared to homogeneous nucleation.
In case of heterogeneous nucleation, due to the presence of active nucleation sites, the barrier to overcome for the nucleation to occur is significantly decreased as shown in figure 1.2. Heterogeneous nucleation being surface assisted or catalyzed nucleation phenomena depends on the contact angle of the nucleus with respect to the substrate. The stronger the wetting of the surface (or small contact angle), the lower the free energy change, and thus will be the lower nucleation barrier energy.\textsuperscript{16} Those nuclei formed on the support surface are no longer spherical but form caps, making spherical contact angle $\theta$ with respect to the supporting surface as shown in figure 1.3. For $\theta \leq \pi$, this will facilitate the heterogeneous nucleation. The critical radius of the nucleus ($r^*$) is same for both the nucleation processes, while the critical volume of nucleus for heterogeneous nucleation is smaller than for homogeneous nucleation. Further, the total free energy required for heterogeneous nucleation is equal to the product of homogeneous nucleation and a function of contact angle ($\theta$).\textsuperscript{21}

$$\Delta G_{het}^* = f(\theta)\Delta G_{hom}^*$$ \hspace{1cm} (1.3)

\textbf{Figure} 1.3. Nuclei making contact angle ($\theta$) during heterogeneous nucleation.
There are various other theories of nucleation and growth mechanism of nanoparticles proposed and explained till date. LaMer\textsuperscript{24-25} proposed a mechanism during the study of synthesis of Sulfur sols from sodium thiosulfate decomposition. LaMer diagram, fig 1.4., explains the process of nucleation and growth in three segments, which is plotted between concentration of monomers versus time. The first segment (I) shows the rapid increase in the concentration of free monomers in the solution. Then, when the monomer concentration stretches to some critical value ($C_{\text{crit}}$), brust nucleation occurs, dropping the concentration of free monomers in solution. This process happens in the second (II) segment, and in this portion the rate of nucleation is considered to be infinite. After this point, further nucleation will not occur due to low concentration of monomers. The third (III) segment shows the growth controlled by the diffusion of the monomers through the solution. The study of growth of silver halides\textsuperscript{26} follows this phenomena of classical nucleation and growth.

\textbf{Figure 1.4.} LaMer diagram explaining nucleation and growth of nanoparticles.\textsuperscript{25}
Another mechanism of nucleation and growth of nanoparticles described was Ostwald ripening,\textsuperscript{27} which explains the growth of nanoparticles caused due to size dependent solubility of NPs. The small particles having higher solubility and surface energy within the solution redissolve facilitating the larger particle growth. The inverse process of this mechanism, called digestive ripening, was introduced by Lee et.al.,\textsuperscript{28} where larger particles disintegrate to allow the smaller particles to grow. Other theories proposed regarding nucleation are Finke-Watzky two step mechanism,\textsuperscript{29} and intraparticle ripening explained by Peng et.al.\textsuperscript{30-31}

Here, during our study, we develop an experimental strategy for monitoring the time-dependent monomer concentration during the hot-injection synthesis of Ag nanoparticles. These colloids were chosen as a model system for studying the nucleation dynamics due to the simplicity of a single-atom monomeric unit. The release of Ag\textsuperscript{0} monomers was achieved in a controllable manner through the thermal decomposition of silver-oleylamine complexes [(R-CH\textsubscript{2}-NH\textsubscript{2}) Ag\textsuperscript{+} [NO\textsubscript{3}]-] fabricated by mixing silver salts (AgNO\textsubscript{3}) with oleylamine. Monitoring of the monomer concentration in the bulk of solution, [Ag\textsuperscript{0}], was then achieved by introducing a small amount of Au nanoparticles into the reaction flask prior to the addition of the silver precursor. The Plasmon resonance of Au NPs is highly sensitive to the addition of Ag\textsuperscript{0} monomer and was used to gauge the Ag monomer concentration. In particular, the precipitation of Ag\textsuperscript{0} on the surface of Au nanoparticles is a diffusion–limited reaction, which causes the Plasmon resonance of 5-nm Au to gradually blue-shift towards the position of the Ag Plasmon resonance (\(\lambda = 415\) nm) at an approximate rate of \(\Delta\lambda = 8.8\) nm per 1 angstrom of the deposited Ag shell (see Fig. 3.2). By monitoring the Plasmon peak of isolated Ag nanocrystals (\(\lambda = 415\) nm) and the blue-shifted resonance of Au (\(\lambda = 490 - 525\) nm) simultaneously, one can deduce the monomer concentration prior to the nucleation burst. Here, the spectral shift of the Plasmon resonance was used to calculate
the critical concentration of Ag\(^0\) needed for the silver nanoparticle nucleation, \([M_{\text{critical}}]\). By measuring the relative concentration of Ag\(^0\) immediately before the nucleation burst, we were able to elucidate the effect of reaction parameters on the rate of nucleation and the ensuing nanoparticle morphology.
CHAPTER II. EXPERIMENTAL METHODS

2.1. Materials

Oleylamine (OLAM, 70%; Aldrich), oleic acid (OA, 90%; Aldrich), Acetone (ACS, Amresco), toluene (anhydrous, 99.8%; Aldrich), octane (anhydrous, 99%; Aldrich), silver nitrate (99%, Sigma- Aldrich), gold(III) chloride (99%, Acros Organics), methanol (anhydrous, 99.8%, Aldrich), ethanol (anhydrous, 95%, Aldrich), and toluene (anhydrous, 99.8%, Aldrich), chloroform (99 %, Sigma Aldrich), hexane (anhydrous, 95%, Aldrich), were used as purchased. All the synthesis were done under argon atmosphere using the standard air free Schlenk technique unless otherwise stated, and the centrifuge used for precipitation rotates at 7200 rpm.

2.2. Synthesis of Au Cores

The synthesis of Au nanocrystals was done by using the procedure developed by Khon et.al.39 For this, 0.011 g AuCl₃ was mixed with 3ml pumped oleylamine (OLAM) in a one-neck flask. The mixture was sonicated for 10-15 minutes such that gold salt was dissolved and the color of mixture changed from transparent yellow to orange due to the formation of Au-oleates. Then, the reaction temperature was increased and kept at 100 ℃ while stirring under argon for 30 minutes. During this time, the reaction mixture color changed from orange to deep purple. It was then cooled to room temperature. The reaction mixture was transformed into two centrifuge tubes, and excess ethanol was added. After that, the tubes were centrifuged for 5 minutes. The clear supernatant was poured off and the precipitate was dissolved in 6 mL chloroform. This cleaning with chloroform/ethanol was repeated. Finally, Au cores were collected in 4 mL of chloroform.
2.3. Synthesis of Oleylamine Capped Au/Ag Heterostructures

The procedure followed for this work was inspired by the procedure reported by Shore et.al.\textsuperscript{32} In our case, 0.2M AgNO\textsubscript{3} solution was prepared separately in deionized water. 5ml of pumped oleylamine was taken in a two-neck 25ml flask with magnetic stirrer. It was heated under argon to the temperature of 110 °C. Then, 20 units of gold cores prepared in the previous step was taken and injected into the flask. Initially, the temperature of the mixture in the flask was decreased below 110 °C, but gradually, it increased and got stable at 110 °C. Before the injection of AgNO\textsubscript{3} solution, all the chloroform was evaporated that was injected along the Au core, which was used to preserve Au cores. Then, the AgNO\textsubscript{3} solution prepared was all injected into the flask and the localized surface plasmon resonance (LSPR) absorption peak was measured every minute. The LSPR peak of nanoparticles (NPs) initially with only Au cores at 525 nm gradually blue-shifted towards the position of pure Ag NPs LSPR peak at 415nm. This process of measuring absorption was done until the nucleation of Ag was seen. In this condition, the absorption peak had two peaks, one close to Au LSPR peak and another close to Ag LSPR peak. After obtaining the Ag nucleation, the reaction mixture was cooled to room temperature. The reaction mixture was transferred to the two centrifuge tubes. Then, excess ethanol was added and centrifuged for 5 minutes. The supernatant was poured off, and the precipitate was collected in 4 mL chloroform. Similar processes were done for 0.126M and 0.03M AgNO\textsubscript{3} solutions. Also, we employed the same procedure to see silver nucleation using 22mM AgNO\textsubscript{3} solution at 110 °C and 0.25mM AgNO\textsubscript{3} solution at 160 °C. All of the absorption profile were recorded for further analysis. The absorption curves were used to map Ag\textsuperscript{0} monomer concentration before actual nucleation of silver took place.
2.4. Synthesis of Oleylamine Capped Ag NPs

For this, 22mM AgNO3 solution was prepared separately in deionized water. 5ml of pumped oleylamine was taken in a two-neck 25ml flask with a magnetic stirrer and was heated under argon to the temperature of 160 °C. Then, the initially prepared AgNO3 solution was injected into the flask and LSPR absorption peak was measured every 2 minutes. An equal amount of sample was taken out of the reacting flask for each absorption measurement. The LSPR peak of silver continued to increase in height until 16 minutes, indicating the saturation of Ag NPs being obtained, due to the conversion of all monomers into nanoparticles. After 16 minutes, the height of the LSPR peak started to decrease. So, after 16 minutes, the reaction was stopped and the mixture was cooled to room temperature. The reaction mixture was transferred to two centrifuge tubes. Then, excess ethanol was added and centrifuged for 5 minutes. The supernatant was poured off, and the precipitate was collected in 4 mL chloroform.

2.5. Synthesis of Oleylamine and Oleic acid Capped Ag NPs

For this, 12mM AgNO3 solution was prepared in deionized water. 4.5 ml pumped oleylamine and 0.5ml Oleic acid was taken in a two-neck 25ml flask with a magnetic stirrer and was heated under argon to the temperature of 160 °C. Then, the initially prepared AgNO3 solution was injected into the flask and LSPR absorption peak was measured every 2 minutes. An equal amount of sample was taken out of the reacting flask for each absorption measurement. The LSPR peak continued to increase in height until 23 minutes, indicating the saturation of Ag NPs being formed, due to the conversion of all monomers into nanoparticles. After 23 minutes, the height of the LSPR peak started to decrease. So, after 23 minutes, the reaction was stopped and the mixture was cooled to room temperature. The reaction mixture was transferred to two centrifuge tubes. Then, excess
ethanol was added and centrifuged for 5 minutes. The supernatant was poured off, and the precipitate was collected in 4 mL chloroform.

2.6. Characterization

UV-vis absorption spectra were recorded using a CARY 50 scan spectrophotometer. High resolution transmission electron microscopy (TEM) measurements were carried out using JEOL 311UHR operated at 300kV. Specimens were prepared by depositing a drop of NP solution in organic solvent onto a carbon-coated copper grid and allowing it to dry in air.
CHAPTER III. RESULTS AND DISCUSSION

We employed a commonly recognized formalism that gives the rate limiting step to the precursor (P) to monomer (M) conversion reaction:\(^10\) \(P \rightarrow M_1\), for the modelling of nanocrystal growth. The monomer unit is defined as the smallest nanoparticle building block carrying a zero electrical charge, and the growth of nanocrystals can then be described as the addition or dissociation of monomers: \(M_n + M_1 \leftrightarrow M_{n+1}\). For example, in the case of CdSe semiconductor NCs, such monomer unit is formed via the initial cation-anion binding reaction followed by the cleavage:\(^9, 33\)

\[
\text{Cd(OOCR)}_2 + \text{SePR}_3 \leftrightarrow [\text{Cd(OOCR)(SePR}_3)]^+ \text{[OOCR]}^- \rightarrow M_1(\text{CdSe}) + \text{OPR}_3 + \text{O(OOCR)}_2 \tag{3.1}
\]

The hot-injection growth of metal nanoparticles follows a similar scheme. Namely, the colloidal synthesis of Ag NPs performed through the thermal dissolution of the Ag-oleylamine complexes involves the same precursor conversion steps:

\[
\text{R-CH}_2\text{-NH}_2 + \text{AgNO}_3 \rightarrow [(\text{R-CH}_2\text{-NH}_2) \text{Ag}]^+ [\text{NO}_3]^- \rightarrow \text{Ag}^0 + \ldots \tag{3.2}
\]

Consequently, both CdSe and Ag nanoparticle nucleation kinetics are driven by similar reaction-limited processes of monomer assembly, which face the energy activation threshold. From the experimental standpoint, however, monitoring the nucleation dynamics of metal nanoparticles is easier to accomplish as this reaction requires the conversion of only one precursor allowing for a more straightforward interpretation of the observed experimental data.

Previous works\(^34-39\) have shown that Ag-oleylamine complexes form immediately upon mixing of silver salt (AgNO\(_3\)) and oleylamine at room temperature, while the thermal conversion of the \(\text{Ag}^+\text{R}^0\text{NH}_2^-\) precursor to a Ag\(^0\) monomer occurs slowly at temperatures above \(T = 70\) °C. The burst
of silver NP nucleation is apparent as the onset of the plasmon resonance at $\lambda = 415$ nm, which occurs in nuclei as small as $d = 1.5$ nm in diameter. The subsequent growth of Ag nanoparticles beyond the critical radius is accompanied by a slight shift of the plasmon resonance towards longer wavelengths.

**Figure 3.1.** (a). Illustration of the basic strategy for monitoring the concentration of the Ag$^0$ monomer during the hot-injection growth of Ag nanoparticles. By introducing a small amount of Au NPs into the growth mixture, the conversion of the Ag precursor (AgNO$_3$) to monomer (Ag$^0$) can be observed as proportional to the red-shift of the Au plasmon resonance, corresponding to the precipitation of Ag$^0$ on Au surface. The rate of the Ag shell growth is then used to estimate the monomer flux in solution, $D \times [M_i] \times L$, where D is the
monomer diffusivity and $[M_1]$ is the monomer concentration. (b) The growth of the Ag shell on Au NPs is investigated for the case when nucleation of isolated Ag NPs is suppressed (due to a low precursor concentration). Although the concentration of the Ag precursor is insufficient to trigger nucleation, it gives rise to an observable shift of the Au plasmon resonance, confirming the diffusion-limited character of this reaction. (c-d). Transmission Electron Microscopy (TEM) images of a typical reaction product containing isolated Ag NPs and large-diameter Au/Ag core/shell dots (e) High resolution TEM image of Au/Ag core/shell nanoparticle showing a single-phase lattice structure.

The two determining factors for growth of nanoparticles are the surface reaction and the monomer’s diffusion to the surface.\textsuperscript{22} The total flux of monomers toward the particle surface is given by:

$$ J = \left( 4\pi r^2 / V_m \right) \frac{dr}{dt} $$ \hspace{1cm} (3.3)

Here $\frac{dr}{dt}$ is a particle growth rate and $V_m$ is the molar volume. According to the nucleation framework proposed by Talapin et.al.\textsuperscript{6}, the nanoparticle growth rate can be expressed as:

$$ \frac{dr}{dt} = V_m D \frac{[M_1] - C^0 \exp\left( \frac{2\gamma V_m}{rRT} \right)}{r + (D/k) \exp\left( \frac{2\gamma V_m}{rRT} \right)} $$ \hspace{1cm} (3.4)

where $D$ is the monomer diffusion, $[M_1]$ is a monomer concentration in the bulk of the solution, $\gamma$ is the surface energy per unit area, $C^0$ is the solubility of the monomer, $k$ is the growth rate constant, $\alpha$ and $\beta$ are transfer coefficients.
Prior to nucleation, the monomer concentration is relatively high, such that the negative term in
the numerator of Eq. 3.4, which reflects the particle dissolution process, can be neglected (see Fig.
3.3). This will allow simplifying the expression for nanoparticle growth rate:

\[
\frac{dr}{dt} = D \times [M_1] \times L,
\]

\[
L = \frac{V_m}{r + (D/k) \exp \left( \frac{2\gamma V_m}{rRT} \right)}
\]

(3.5)

To monitor the relative concentration of \( \text{Ag}^0 \) monomers in the reaction mixture, a small amount of
Au nanoparticles was added to the oleylamine solution of the AgNO\(_3\) precursor. In this case, the
thermal conversion of AgNO\(_3\) to Ag\(^0\) was accompanied by the spectral shift of the Au plasmon
absorption due to the precipitation of neutral silver on Au surfaces (see Fig. 3.1a). Previous works
have shown that the plasmon resonance of Au/Ag core/shell system lies in between of those of
isolated Au and Ag. In particular, one recent study\(^{32}\) has demonstrated that the spectral position of
the Au/Ag NP plasmon resonance is a simple function of the Au volume fraction, \( \nu_{\text{Au}} \):

\[
\lambda_{\text{Au}/\text{Ag}}^{\text{plasmon}} \approx \nu_{\text{Au}} \lambda_{\text{Au}}^{\text{plasmon}} + (1 - \nu_{\text{Au}}) \lambda_{\text{Ag}}^{\text{plasmon}} = 525 \times \left( \frac{R_{\text{Au}}}{R_{\text{Au}/\text{Ag}}} \right)^3 + 420 \times \left[ 1 - \left( \frac{R_{\text{Au}}}{R_{\text{Au}/\text{Ag}}} \right)^3 \right]
\]

(3.6)

When the thickness of the Ag shell is relatively small, the resonant wavelength, \( \lambda_{\text{Au/Ag}} \), can be
approximately expressed as a linear fit of the Ag shell thickness, \( \Delta r_{\text{Ag}} \):

\[
\lambda_{\text{Au}/\text{Ag}}^{\text{plasmon}} (\text{nm}) \approx \alpha \times \Delta r_{\text{Au}/\text{Ag}} (\text{nm}); \quad \alpha = 88
\]

(3.7)

Experimental evidence of both homogeneous and heterogeneous growth of Ag is provided by the
characteristic TEM images of a reaction product in Figs. 3.1(c)-(e), which confirms the presence
of both isolated Ag NPs and Au/Ag core/shell heterostructures. The two different morphologies are readily distinguishable by their sizes as well as the darker contrast of a heavier Au phase.

**Figure 3.2.** The expected relation between the spectral position of the Au/Ag core/shell plasmon resonance and the thickness of the Ag shell, calculated from Eq. 3.6 ($d_{Au} = 5$ nm). For small values of the Ag shell thickness, the spectral shift of the plasmon resonance is roughly linear.

According to Fig. 3.2, the rate of $Ag^0$ addition onto Au is proportional to the monomer flux in the solution and is assessable as a blue shift of the Au/Ag core/shell Plasmon resonance. Notably, the heterogeneous growth of a silver shell has a relatively low activation energy as lattices of Ag and Au fcc phases are nearly matched (strain = 0.24%). Consequently, we expect that the Ag shell growth is diffusion-limited, such that $Ag^0$ monomers start to attach to the surface of Au NPs as soon as the AgNO$_3$ precursor conversion begins. To confirm this statement, Au nanoparticles were heated in the presence of the silver precursor at concentrations that were significantly below the
Ag NP nucleation threshold. Expectedly, the growth of isolated Ag nanoparticles was not observed in this case (Fig. 3.1.b). Nevertheless, the Plasmon resonance of Au NPs has gradually blue-shifted with the increasing temperature, indicating that the precipitation of Ag⁰ began simultaneously with the precursor conversion (see Fig. 3.1.b). This tendency implies that the energy activation barrier for the shell growth reaction is negligibly small. Further evidence of the “low-barrier” growth of the Ag shell is provided by the TEM images of core/shell heterostructures which confirm a uniform distribution of the Ag shell around the Au core (Figs. 3.1c-3.1e), consistent with low strain between the two phases. For instance, a single-phase growth of the core/shell structure can be seen in a high resolution TEM image of a characteristic Au/Ag nanoparticle (Fig. 3.1e).

Figure 3.3. Evolution of the plasmon resonance in Au/Ag core/shell nanoparticles corresponding to (a) growth of the shell in the presence of AgNO₃ precursor (T = 110 °C),
(b) thermal dissolution of the Ag shell (T = 110 °C). The process of dissolution appears to be much slower.

An important goal of this study lies in unveiling the relationship between the critical concentration of the Ag monomer, \( [M_1^{\text{critical}}] \), and reaction variables including the solvent temperature and the concentration of ligand molecules in solution. To reach this goal, we rely on the nucleation theory framework to obtain a systematic approach for extracting a relative concentration of Ag monomer in solution, \( [M_1] \), from the spectral shift of the plasmon resonance in Au/Ag core/shell NPs. To simplify the analysis, we assume that prior to the nucleation of Ag NPs, the Ag\(_0\) monomer concentration in solution is sufficiently high to ensure that the growth of the Ag shell is much faster than its dissolution (\( \Delta r_{\text{dissolution}}^{\text{Au/Ag}} < 1 \) nm/min; \( \Delta r_{\text{growth}}^{\text{Au/Ag}} >> 1 \) nm/min, see Fig. 3.3). This assumption allows introducing two important generalizations. First, the reduction in the Ag layer thickness on Au surfaces due to Ag\(_0\) dissolution back into solvent can be neglected. Second, the monomer concentration in the bulk of the solution, \( [M_1] \), and near the surface of the nanoparticles, \( [M_s] \), are approximately the same, \( [M_1] \approx [M_s] \). As a result, the rate of Au/Ag core/shell nanoparticle growth can be expressed as a linear function of the monomer concentration\(^6 [M_1] \), as derived in Eq. 3.5.

\[
\frac{dr}{dt} = D \times [M_1] \times L(r, C^0, \gamma) \tag{3.8}
\]

which takes into the account the diffusion of the monomer, \( D \), and the monomer concentration in solution, \( [M_1] \). The constant \( L \) is a complex function of nanoparticle radius (\( r \)), surface tension (\( \gamma \)), and monomer solubility (\( C^0 \)).
Figure 3.4(a). Illustration of the experimental strategy for measuring the relative concentration of Ag\(^0\) monomer in solution. If the solvent temperature is kept constant, the pre-nucleation monomer concentration \([M_1]\) increases linearly with time (provided that \([M_1] \ll [P]\)). The accumulative growth of the Ag shell on Au, \(\Delta r_{Au/Ag}\), can then be expressed proportionally to the area under the \([M_1(t)] = k[P]\) curve.(b). The ratio of the two \(\Delta r_{Au/Ag}\) values corresponding to two different precursor concentration, \([P_1]\) and \([P_2]\), are independent of D and L parameters and is determined only by the nucleation time.
According to Eq. 3.8, the rate of the Au/Ag core/shell nanoparticle growth, \( \frac{dr_{Au/Ag}}{dt} \), is proportional to the monomer concentration at any given moment during the reaction, \( [M_1(t)] \). This approximation is derived using a single assumption that rate of Au/Ag NP dissolution during the pre-nucleation reaction stage, \( t < t_{nucl} \), is relatively small and can be neglected. Generally, the shell growth rate, \( \frac{dr_{Au/Ag}}{dt} \), should be calculated from a characteristic blue-shift of the plasmon resonance, \( \Delta \lambda_{Au/Ag}^{plasmon} \), during a short time interval, \( dt \): 

\[
\lambda_{Au/Ag}^{plasmon}(t + \Delta t) - \lambda_{Au/Ag}^{plasmon}(t).
\]

Experimentally, however, measuring the instantaneous changes in the position of the plasmon resonance can be difficult. As an alternative, we have developed a simplified formalism that allows estimating the relative
monomer concentrations \([M_1(t)]\) from the overall shift of the Au/Ag plasmon resonance. This approach is illustrated in Fig. 3.4. Prior to the nucleation of Ag NPs, the monomer concentration \([M_1]\) in solution is steadily growing due to the thermal conversion of the precursor \((\text{AgNO}_3 \rightarrow \text{Ag}^0)\). If the solvent temperature is maintained at the same value, the precursor decomposition can be assumed to proceed at a constant rate, \(k\), \(d[P] = -k[P]dt\). In this case, the monomer concentration can be expressed as: \([M_1] = [P](1 - e^{-k(T)t})\). Simply, during the initial stages of the reaction (see Fig.3.5), we can write

\[
[M_1]_{M_1 \ll P} = [P]kt
\] (3.9)

During the total reaction time, the accumulative growth of the Ag shell, \(\Delta r_{\text{Au/Ag}}\) will be determined by the total flux of \(\text{Ag}^0\) monomer to the Au surface which is proportional to the area under the \([M_1(t)]\) curve, as illustrated in Fig. 3.4a. Namely, according to Eq. 3.8:

\[
\Delta \lambda_{\text{plasmon}}^{\text{Au/Ag}} \sim \alpha \Delta r_{\text{Au/Ag}} (T = \text{const}) = \int_0^{t_{\text{nuc}l}} (D \times k[P]t \times L) dt = D \times L \times \frac{M_1^{\text{critical}}}{2} t_{\text{nuc}l}
\] (3.10)

Consequently, the critical concentration of the monomer can be expressed as a linear function of the Plasmon shift: \(M_1^{\text{critical}} \sim \Delta \lambda_{\text{plasmon}}^{\text{Au/Ag}} / (D \times L \times t_{\text{nuc}l})\). Notably, when the critical concentration is investigated through the comparison of the two reactions, A and B, featuring either different temperatures, \(T_A\) and \(T_B\), or ligand densities, the constant \(L\) can often be omitted:

\[
\frac{M_1^{\text{critical}}(A)}{M_1^{\text{critical}}(B)} \approx \frac{\Delta \lambda_{\text{plasmon}}^{\text{Au/Ag}}(A)}{\Delta \lambda_{\text{plasmon}}^{\text{Au/Ag}}(B)} \times \frac{D(B) \times t_{\text{nuc}l}(B)}{D(A) \times t_{\text{nuc}l}(A)} \approx \frac{\Delta \lambda_{\text{plasmon}}^{\text{Au/Ag}}(A)}{\Delta \lambda_{\text{plasmon}}^{\text{Au/Ag}}(B)} \times \frac{T_B \times t_{\text{nuc}l}(B)}{T_A \times t_{\text{nuc}l}(A)}
\] (3.11)

In the last step, we assumed that the monomer diffusion \(D\) scales linearly with temperature:

\(D(T_1)/D(T_2) = T_1/T_2 \times (\nu_2/\nu_1)\), where \(\nu\) is the viscosity of the solvent.
The validity of Eq. 3.11 can be illustrated through the comparison of the two nucleation reactions, A and B, featuring high and low concentrations of the AgNO₃ precursor, respectively. In both cases, the nucleation of Ag NPs is induced by injecting the AgNO₃ salt, dissolved in a minimal amount of water, into a hot oleylamine (T = 110 °C). If syntheses A and B are run at the same temperature, the nucleation of Ag NPs in flask A (high-concentration) will occur faster due to an earlier buildup of the critical monomer concentration (see Fig. 3.4b). Notably, the nucleation is expected to occur at the same value of $[M_1^{critical}]$ for both reactions, $[M_1^{critical}]_A = [M_1^{critical}]_B$, which follows directly from Eq. 3.8, since $D_A = D_B$ and $L_A = L_B$. Consequently, the shift of the plasmon resonance, according to Eq. 3.11, should be simply proportional to the nucleation time (see Fig. 3.4b):

$$\frac{\Delta \lambda^{plasmon}_{Au/Ag}(A)}{\Delta \lambda^{plasmon}_{Au/Ag}(B)} \approx \frac{t_{nuc}(A)}{t_{nuc}(B)}$$

These expectations are corroborated by the absorption kinetics of several shell growth reactions (Fig. 3.6), performed at the same solvent temperature (T= 110 °C). By using different concentrations of the Ag precursor for the three cases, we were able to achieve substantially different times of Ag NP nucleation (Fig. 3.6a-c). The overall shift of the Au/Ag plasmon resonance was then recorded at the time of the nucleation event and plotted versus the nucleation time in Fig 3.6d. As expected from Eq. 3.12, the blue-shift of the Au/Ag plasmon resonance was found to increase with the nucleation time. Based on a reasonable agreement of the least-square fit to the experimental data in Fig. 3.6d, we conclude that the value of the shift grows linearly with $t_{nuc}$, as predicted by Eq. 3.12.
Figure 3.6. Validating the linearity of the Au/Ag plasmon shift with nucleation time (according to Eq. 3.12). The thermal decomposition of the AgNO₃ precursor in the presence of Au NPs is performed at different precursor concentrations: (a) [P] = 0.03 M (b) [P] = 0.126 M (c) [P] = 0.2 M, causing the nucleation reaction to occur at different times. All of the displayed reactions were performed at T = 110 °C. Consistently with Eq. 3.11, the blue-shift of the Au/Ag plasmon resonance increases with increasing nucleation time. (d). Time-dependence of the pre-nucleation blue-shift of the Au/Ag plasmon resonance. A straight line represents a linear fit to the experimental data.

We now apply the developed strategy towards studying the temperature dependence of the nucleation rate. An important question to be addressed is whether the critical monomer concentration required for nanoparticle nucleation, \([M_{i}^{\text{critical}}]\), depends on the reaction temperature. Thus far, qualitative models of nucleation have limited the temperature dependence to the precursor conversion reaction only¹⁰ omitting the secondary effect of the reaction temperature on the probability of nuclei formation. In the meantime, the existence of an activation barrier, \(\Delta E\), for
the nuclei growth implies that the nucleation rate may be affected by the solvent temperature, depending on the exact balance between the monomer kinetic energy and the height of the activation barrier, \(\exp(-\Delta E/k_BT)\).

To investigate the effect of the reaction temperature on the value of \([M^{critical}_1]\), we have compared the dynamics of Ag nanoparticle nucleation at \(T = 110 \, ^\circ C\) and \(T = 160 \, ^\circ C\). Solvent temperatures above 100 \(^\circ C\) were chosen to prevent the reaction of Ag clusters with water, which may cause oxidation of the surface ions. To measure the critical monomer concentration, the two reaction mixtures comprising pumped oleylamine were heated to respective temperatures and loaded with equal amounts of Au NPs. A few minutes were then allowed for the evaporation of Au NP transfer solvent (chloroform), which resulted in a recovery of the reaction temperature. The Ag nanoparticle growth was then initiated by injecting a small amount of a concentrated AgNO\(_3\) precursor in water (about 0.2ml), starting the reaction clock. The injection was performed without submerging a needle tip into a hot solvent to help avoiding premature heating of the Ag precursor.

The evolution of the absorption spectra corresponding to the Ag NP nucleation at \(T = 110 \, ^\circ C\) and \(T = 160 \, ^\circ C\) is analyzed in Fig. 3.7. The precursor concentrations for the two reaction mixtures were adjusted to \([P_{110}] = 22 \, mM\) and \([P_{160}] = 0.25 \, mM\) to promote similar nucleation times. This allowed establishing similar rates of the precursor-to-monomer conversion in both flasks: \(k_{110}[P_{110}] = k_{160}[P_{160}]\) (see Eq. 3.9), whereby excluding the non-linear effects associated with monomer evolution \([M_1(t)]\) at different temperatures. Furthermore, similar reaction times allowed minimizing the potential discrepancy between \(\Delta r_{110}\) and \(\Delta r_{160}\) values, which may arise due to uneven contributions of the shell dissolution processes. According to Fig. 3.7, critical concentrations of the Ag monomer in both reaction mixtures were reached at approximately the
same time, $t_{\text{nucl}} \approx 4$ min. Consequently, according to Eq. 3.11, the ratio of the critical monomer concentrations at the two temperatures could be expressed as:

$$\frac{M_1^{\text{critical}} (110 \, ^\circ \text{C})}{M_1^{\text{critical}} (160 \, ^\circ \text{C})} \approx \frac{\Delta \lambda_{\text{plasmon}}^{\text{Ag/Au}} (110 \, ^\circ \text{C})}{\Delta \lambda_{\text{plasmon}}^{\text{Ag/Au}} (160 \, ^\circ \text{C})} \times \frac{433 K}{383 K} \times \frac{t_{\text{nucl}}^{(160)}}{t_{\text{nucl}}^{(110)}} = \frac{27 \text{ nm}}{34 \text{ nm}} \times \frac{433 K}{383 K} = 0.9 \quad (3.13)$$

Figure 3.7. Ag nanoparticle nucleation kinetics observed at two different solvent temperatures: (a). $T = 110 \, ^\circ \text{C}$ and (b). $T=160 \, ^\circ \text{C}$. The concentrations of AgNO$_3$ precursor were adjusted to $[P_{110}] = 22$ mM and $[P_{160}] = 0.25$ mM in order to promote similar nucleation times ($t_{\text{nucl}} \approx 4$ min). In this case the ratio of the critical monomer concentrations at the two temperatures can be obtained from the absorbance data using Eq. 3.13.

The comparison of the two reactions at $T = 110 \, ^\circ \text{C}$ and $T = 160 \, ^\circ \text{C}$ reveals an interesting fact: the spectral shifts of plasmon resonances in the two cases are almost the same despite markedly different monomer conversion rates, $k[P_{110}]/k[P_{160}] \approx 90$. The Ag nucleation in the high-temperature flask was accompanied by a slightly larger plasmon shift ($\Delta \lambda_{160} = 34 \, \text{nm}$ versus $\Delta \lambda_{110} = 27 \, \text{nm}$).
which can be attributed to an enhanced monomer diffusion at \( T = 160 \, ^\circ\text{C} \): \( D_{160}/D_{110} \approx (433K/383K) \times (v_{110}/v_{160}) \) reflecting the larger temperature and the decreased viscosity of the solvent. This data strongly suggests that critical concentrations of the monomer required for nucleation at \( T = 110 \, ^\circ\text{C} \) and \( T = 160 \, ^\circ\text{C} \) are near parity! Indeed, \( [M_1^{\text{critical}}]_{110}/[M_1^{\text{critical}}]_{160} = 0.9 \) does not take into account the solvent viscosity change, which may further increase this ratio, bringing it closer to unity. Based on the near matching values of \( [M_1^{\text{critical}}] \), we propose that the monomer concentration required for nucleation is independent of the reaction temperature. This result is not immediately apparent from the nucleation theory (Eq. 3.4). Classically, the solvent temperature defines the monomer kinetic energy, which is used to overcome the activation barrier for changing the solute/nucleus chemical potential. The observed temperature-independence of \( [M_1^{\text{critical}}] \) may imply that both reactions occur in the over barrier region, namely, monomers carry sufficient kinetic energy to clear the chemical potential barrier. This explanation is also consistent with the fact that the nucleation of Ag NPs is readily observed even at room temperatures.

We now turn our attention to the effect of surface ligands on the critical monomer concentration. Previous works have demonstrated an important role of the precursor chemistry in the nanocrystal nucleation dynamics. It was shown that low reactive precursors (e.g. phosphonic / phosphinic acid derived metal precursors) delay the formation of monomers allowing only a small fraction of clusters with sizes above the critical radius to grow.\(^{40}\) This promotes large nanoparticle diameters and poor size distributions. On the contrary, high reactivity precursors (e.g. bis(trimethylsilyl) chalcogenides and short chain alkyl metal complexes) enable high monomer concentrations which triggers the fast onset of nucleation. This results in low mean nanoparticle diameters.
Figure 3.8. Comparison of the Ag nucleation dynamics for the two reactions featuring ligand-saturated (OLAM only) and ligand-deprived (OLAM:OA = 1:9) growth conditions. (a,c). Evolution of the Au/Ag plasmon absorption for the OLAM-only synthesis ([P(AgNO₃)OLAM] = 22 mM, T = 160 °C) results in a large, 27-nm, blue shift of the plasmon resonance and low mean nanoparticle diameter, $d_{av} = 4.9$ nm. (b,d). Evolution of the Au/Ag plasmon absorption for the OLAM/OA synthesis ([P(AgNO₃)OLAM/OA] = 12 mM, T = 160 °C) results in a much smaller, 3-nm, blue shift of the plasmon resonance and a larger nanoparticle diameter, $d_{av} = 14.6$ nm.

While the effect of the precursor chemistry on the evolution of nanoparticle shapes has been investigated extensively, the role of ligands in the process of an energy-activated cluster assembly
is still unclear. One of the questions that demands attention is whether the concentration of free ligands in solution can affect the monomer nucleation rate. To address this issue, we have looked for characteristic changes in the value of $M_{i}^{\text{critical}}$ induced by variations in the primary ligand concentration. A typical synthesis of Ag NPs is performed in oleylamine (OLAM), which serves a dual role of the reaction solvent and the L-type $^{41}$ (neutral donor) surface ligand. Consequently, the growth reaction is performed in a ligand-saturated solution, where neutral monomers Ag$^0$ can form complexes with OLAM molecules. Reducing the concentration of an OLAM ligand in this case can be achieved by diluting the reaction mixture with a hydrocarbon solvent or an X-type ligand. In this work, we employ electron-donating oleic acid (OA) molecules, which negatively charge ([OOCR]$^-$) prevents the formation of monomer-ligand complexes. As a result, OA acts primarily as a high-temperature solvent, such that the addition of OA to the reaction mixture simply reduces the concentration of primary ligand (OLAM).

To understand the effect of the ligand concentration on $M_{i}^{\text{critical}}$, we have compared the nucleation kinetics of the two reaction mixtures featuring ligand-saturated (OLAM only) and ligand-deprived (OLAM:OA = 1:9) growth conditions. The concentration of Ag precursors were adjusted to $[P(\text{AgNO}_3)_{\text{OLAM}}] = 22$ mM and $[P(\text{AgNO}_3)_{\text{OLAM/OA}}] = 12$ mM to promote similar nucleation times. In this case, the plasmon shift, $\Delta \lambda_{\text{Au/Ag}}$, is simply proportional to the critical monomer concentration, $\Delta \lambda_{\text{plasmon}}^{\text{Au/Ag}} \sim [M_{i}^{\text{critical}}]$, which follows from Eq. 3.11 assuming that $T_A = T_B$ and $t_{\text{nuc}(A)} = t_{\text{nuc}(B)}$.

According to Fig. 3.8a, the nucleation of Ag NPs in a OLAM/OA mixture leads to a comparatively smaller blue-shift of the Au/Ag plasmon resonance ($\Delta \lambda_{\text{OLAM}} = 27$ nm \textit{versus} $\Delta \lambda_{\text{OLAM/OA}} = 3$ nm). The observed difference between the two growth environments is substantial to indicate that the
ligand-deprived (OLAM/OA) environment requires a lower concentration of Ag monomer for nucleation. Based on Eq. 3.11, we estimate that $[M_i^{\text{critical}}]_{\text{OLAM/OA}} = \frac{1}{9} [M_i^{\text{critical}}]_{\text{OLAM}}$. The suppressed nucleation of Ag in OLAM-only reaction can be attributed to excessive binding of OLAM molecules to a neutral monomer, Ag$^0$. This interaction is possible through a donor-acceptor mechanism, which is facilitated by an apparent oversaturation of OLAM. When the concentration of an L-type OLAM ligand in solution is lowered through the addition of OA, a smaller fraction of monomeric units will be ligated. As a result, cluster nucleation will not require ligand displacement and may go via a simple monomer addition. Likewise, unligated monomers will experience less stearic hindrance, depressing the nucleation barrier.

In addition to affecting the nucleation rate, the concentration of free ligand in solution was found to play an important role in the ultimate morphology of Ag nanoparticles. This was observed by mapping the evolution of Ag NP shapes in OLAM/OA and OLAM-only syntheses. Here, the two reactions were allowed to proceed until the near-complete conversion of the precursor, which was manifested by the saturation of the Ag plasmon absorbance. The two products were then compared using the TEM analysis. According to Figs. 3.8c and 3.8d, nanoparticles grown under ligand deprived (OLAM/OA) growth conditions were larger in size and showed less homogeneity. The observed morphology was consistent with a lower-energy nucleation threshold expected in this case due to a high concentration of unligated, free Ag monomers. Conversely, a large nucleation threshold corresponding to ligand saturated growth (OLAM-only) lead to a comparatively smaller nanoparticle size (see Fig. 3.8c). In such environment most surface sites are terminated with OLAM molecules, suppressing the nanoparticle growth. This highlights an important property of nucleation it is ligand-dependent.
CHAPTER IV. CONCLUSION

We have developed an experimental strategy for estimating the monomer concentration during the hot-injection synthesis of Ag nanocrystals. The thermal conversion of the silver nitrate precursor to a neutral monomer was inferred from the spectral changes in the plasmon resonance of Au nanoparticles that were placed into the reaction flask prior to the precursor injection. It was shown that precipitation of Ag on Au surfaces is a diffusion-limited reaction which causes the plasmon resonance to blue shift at an approximate rate of 9 nm per 0.1 nm of added Ag on the 5nm Au cores. By measuring the relative concentration of Ag$^0$ immediately before the nucleation burst, we were able to elucidate the effect of reaction parameters on the rate of nucleation and the ensuing nanoparticle morphology. In particular, we show that the critical monomer concentration, required for the nucleation to occur, is independent of the solvent temperature; however, it is affected by the concentration of the surface ligand in solution.
REFERENCES


