Kinetics of ligand mediated ultra-small silver cluster formation

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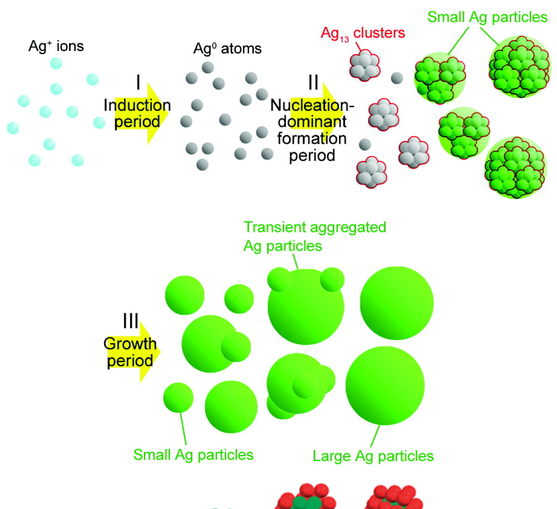
Abstract

Ultra-small Ag nanoparticles are metastable in solution[1] and porous media[2]. Experimental and theoretical studies show that a Ag cluster of diameter 0.7 nm corresponds to a first full-shell Ag_{13}, with icosahedral symmetry[3,4]. This is one of the magic numbers for Ag clusters. We have investigated two kinetic mechanisms that produce different size distributions of silver clusters with a peak diameter around 0.7 nm in solution in the presence of ligands. We first assume ligand mediated growth occurs through dimerization, followed by monomer addition to the seed cluster. In the second scheme we incorporated coalescence which dominates the growth of silver clusters in the presence of a strong reductant. This provides further insight into the mechanistic details of ultra-small silver cluster formation from an atomic perspective. It involves fast precursor conversion of silver ions to monomers stabilized by ligands, followed by ligand mediated growth via monomer addition and coalescence.

Silver cluster formation

A



B

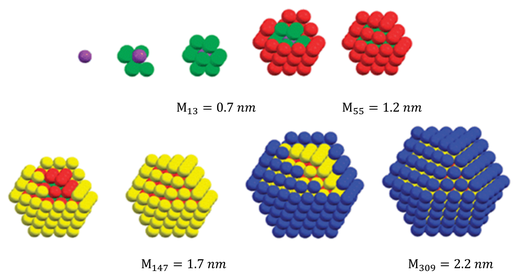


Figure 1. (A) Examples of nanoparticle formatiion[1]. (B) Full-shell metal clusters and their estimated sizes[5].

Model: Kinetic Reaction Scheme 1

Assume the following kinetic steps in a reaction containing a well mixed solution of Ag^+ ions and ligands.

$\boldsymbol{p} \xrightarrow{k_p} \boldsymbol{M}$; Ag+ ion precursor (*p*) conversion to monomers (*M*) of Ag atoms.

$\boldsymbol{M + L} \underset{k_{e1,j}}{\overset{k_{a1,i,j}}{\rightleftharpoons}} \boldsymbol{ML}$; ligand (*L*) association and dissociation with monomers.

$\boldsymbol{2ML} \xrightarrow{k_n} \boldsymbol{P_{2,2}}$; irreversible dimerization ($P_{2,2}$).

$\boldsymbol{P_{i,j} + ML} \underset{k_{d,j+1}}{\overset{k_{g,i,j}}{\rightleftharpoons}} \boldsymbol{P_{i+1,j+1}}$; reversible growth through monomer addition.

$\boldsymbol{P_{i,j} + L} \underset{k_{e2,j+1}}{\overset{k_{a2,i,j}}{\rightleftharpoons}} \boldsymbol{P_{i,j+1}}$; reversible ligand association/elimination with clusters.

Rate constants depend on number of available sites ($N_{s,i}$) and ligands (j) on cluster $P_{i,j}$[6]:

$$k_{g_{i,j}} = k_g(N_{s,i} - j) \qquad k_{d_{i,j}} = k_d j$$
$$k_{a2_{i,j}} = k_{a2}(N_{s,i} - j) \qquad k_{e_{i,j}} = k_e j$$

The rate equation of i-sized cluster with j ligands, $P_{i,j}$ is:

$$\frac{d}{dt}[P_{i,j}] = -k_g[ML][P_{i,j}](N_{s,i} - j) + k_g[ML][P_{i-1,j-1}](N_{s,i-1} - j + 1) + k_d[P_{i+1,j+1}](j+1) - k_d[P_{i,j}]j - k_{a2}[L][P_{i,j}](N_{s,i} - j) + k_{a2}[L][P_{i,j-1}](N_{s,i} - j + 1) + k_{e2}[P_{i,j+1}](j+1) - k_{e2}[P_{i,j}]j$$

Solving 2-D equation is hard. Therefore, we used the method of moments[6] to convert a 2-D equation to two 1-D equations:

$$[\overline{P_i}] = \sum_{j=0}^{\infty}[P_{i,j}], \qquad [\overline{L_i}] = \sum_{j=0}^{\infty} j[P_{i,j}], \qquad [\overline{\overline{L_i}}] = \sum_{j=0}^{\infty} j^2[P_{i,j}]$$

The two 1-D equations, after applying the method of moments are:

$$\frac{d}{dt}[\overline{P_i}] = -k_g[ML]([\overline{P_i}]N_{s,i} - [\overline{L_i}]) + k_g[ML]([\overline{P_{i-1}}]N_{s,i-1} - [\overline{L_{i-1}}]) + k_d([\overline{L_{i+1}}] - [\overline{L_i}])$$

$$\frac{d}{dt}[\overline{L_i}] = -k_g[ML]([\overline{L_i}]N_{s,i} - [\overline{\overline{L_i}}]) + k_g[ML]([\overline{L_{i-1}}](N_{s,i-1} - 1) + [\overline{P_{i-1}}]N_{s,i-1} - [\overline{\overline{L_{i-1}}}]) + k_d([\overline{\overline{L_{i+1}}}] - [\overline{L_{i+1}}]) - k_d[\overline{\overline{L_i}}] + k_{a2}[L]([\overline{P_i}]N_{s,i} - [\overline{L_i}]) - k_{e2}[\overline{L_i}]$$

$[\overline{P_i}]$ represents the concentration of clusters with i monomers regardless of the number of ligands, j. $[\overline{L_i}]$ is the average ligand concentration on a cluster with i monomers. To calculate the shape of this distribution $[\overline{\overline{L_i}}]$, it is assumed that the distribution of j ligands on cluster size i is binomial. With this assumption,

$$[\overline{\overline{L_i}}] = [\overline{L_i}](1 - p_i + N_{s,i}p_i) \qquad \text{where} \qquad p_i = \frac{[\overline{L_i}]}{[\overline{P_i}]N_{s,i}}$$

The 1-D equations were solved numerically using MATLAB. The $\overline{P_i}$(t) distribution is considered as a continuous distribution $P(D,t)$ and converted[6] from a dimensionless mass distribution $P(x,t)$ to a size distribution $P(D,t)$:

$$P(D,t) = 3\frac{0.45^{\frac{1}{3}}}{D_M}x^{\frac{2}{3}}P(x,t)$$

The kinetic parameters were obtained by fitting the distribution to a log normal distribution with a mode of 0.7 nm and standard deviation of 0.2 nm using a genetic algorithm with the following fitness function:

$$Fittness\ Fuction = \left|\frac{\mu_{pdf} - \mu_{model}}{\mu_{pdf}}\right| + \left|\frac{\sigma_{pdf} - \sigma_{model}}{\sigma_{pdf}}\right| + \left|\frac{\max(P(D)_{pdf}) - \max(P(D)_{model})}{\max(P(D)_{pdf})}\right|$$

The ratio of ligand to metal concentration was 120:1.

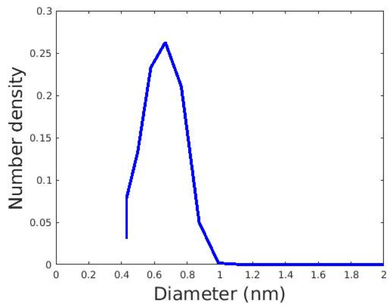


Figure 2. Size distribution of clusters produced by scheme1.

Table 1

k_p	6.12×10^3	1/s
k_{a1}	34.10	1/(M·s)
k_{e1}	9.80×10^{-5}	1/s
k_n	6.39	1/(M·s)
k_{a2}	6.43×10^{-3}	1/(M·s)
k_{e2}	8.73×10^2	1/s
k_g	1.07×10^2	1/(M·s)
k_d	5.94×10^{-4}	1/s

Table 1. Selected rate constants.

In the kinetic reaction scheme 1 we have produced a cluster size distribution of Ag atoms around a magic number diameter of 0.7 nm without considering coalescence.

Model: Kinetic Reaction Scheme 2

Growth occurs also through coalescence of clusters which further affects the shape of the distribution. Therefore we incorporated coalescence in scheme 2, and added the following step:

$$\boldsymbol{P_{i,j} + P_{k,l} \xrightarrow{k_{c,i,k}} P_{i+k} + (j+l)L}$$

We used the Smoluchowski equation to derive the following rate equation for $P_{i,j}$:

$$\frac{d}{dt}[P_{i,j}] = (\text{scheme1 equations}) - k_c\sum_{k=n}^{k_{max}}\sum_{l=0}^{N_{s,k}}[P_{i,j}](N_{s,i} - j)[P_{k,l}](N_{s,k} - l) + \frac{1}{2}k_c\sum_{w+y=i}\sum_{x,z}[P_{w,x}](N_{s,w} - x)[P_{y,z}](N_{s,y} - z)$$

After applying the method of moments to obtain the rate equations for $\overline{P_i}$ and $\overline{L_i}$:

$$\frac{d}{dt}[\overline{P_i}] = (\text{scheme1 equations}) + k_c([\overline{P_i}]N_{s,i} - [\overline{L_i}])\sum_{k=0}^{k_{max}}([\overline{P_k}]N_{s,k} - [\overline{L_k}]) + \frac{1}{2}k_c\sum_{w+y=i}([\overline{P_w}]N_{s,w} - [\overline{L_w}])([\overline{P_y}]N_{s,y} - [\overline{L_y}])$$

$$\frac{d}{dt}[\overline{L_i}] = (\text{scheme1 equations}) - k_c([\overline{L_i}]N_{s,i} - [\overline{\overline{L_i}}])\sum_{k=0}^{k_{max}}([\overline{L_k}]N_{s,k} - [\overline{\overline{L_k}}])$$

Then the rate constant kc was varied while using the rate constants from scheme 1 to produce an optimal fit.

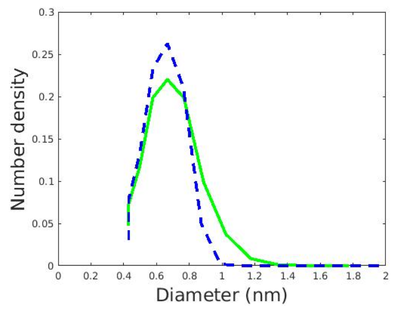


Figure 3. Comparison of the cluster size distributions produced by scheme 2 (green line) with scheme 1 (blue dash line).

Table 2

k_p	6.12×10^3	1/s
k_{a1}	34.10	1/(M·s)
k_{e1}	9.80×10^{-5}	1/s
k_n	6.39	1/(M·s)
k_{a2}	6.43×10^{-3}	1/(M·s)
k_{e2}	8.73×10^2	1/s
k_g	1.07×10^2	1/(M·s)
k_d	5.94×10^{-4}	1/s
k_c	8×10^{-5}	1/(M·s)

Table 2. Selected rate constants.

Conclusions

- To produce ultra-small clusters, fast precursor conversion to monomers must occur in a well mixed solution.
- Ligand adsorption stabilizes and controls the growth rate of clusters, and as a result, metastable ultra-small Ag clusters have a longer lifetime under initial conditions that promote ligand adsorption. Therefore, the ligand concentration should be much greater than the metal.
- Coalescence of clusters, besides monomer addition, plays an important role in the growth of nanoparticles.

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