Electronic Supporting Information

Simulated Annealing Fitting: A Global Optimization Method for Quantitatively Analyzing Growth Kinetics of Colloidal Nanoparticles

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Section I: In situ experiment details on the synthesis of Ag nanoparticles

A in situ microwave reactor compatible with the high-energy synchrotron x-ray beamline was used to probe the evolution of colloidal Ag nanoparticles from microwave-assisted polyol reduction of silver nitrate at controlled temperatures. The recorded time-dependent high-energy x-ray diffraction (HEXRD) patterns were reported in our previous *Nano Letters* paper published in 2016.¹ The experimental details are described in the following.

Chemicals and synthesis. Silver nitrate (AgNO₃), ethylene glycol (EG), polyvinylpyrrolidone (PVP, $M_w \approx 55\,000$, K-30) were purchased from Sigma-Aldrich. In the synthesis, microwave heating was used to control the temperature of reaction solution. PVP was used as surface capping ligands to stabilize the synthesized Ag nanoparticles. Colloidal Ag nanoparticles were synthesized from the reduction of AgNO₃ in EG at elevated temperatures. In a typical synthesis, a 6-mL EG solution containing 0.10 M AgNO₃ and 0.15 M PVP (based on the repeating unit) was loaded to a 10-mL microwave reaction vessel. The reaction mixture was heated by microwave radiation from room temperature to a desired temperature (e.g., 130 °C, 140 °C, 160 °C, 180 °C in the experiment)

at a temperature ramp rate of ~ 20 °C/min, and the temperature was then maintained at the desired temperature for 35 minutes to complete the growth of Ag nanoparticles. After synthesis, the reaction solution was quickly cooled by flowing the pressurized air.

Instrumentations. Figure S1 shows a schematic illustration of the in situ experiment setup. The in situ microwave reactor was placed at 1 ID-E beamline at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), which provided an incident x-ray beam with a photon energy of 70 keV (wavelength = 0.1771 Å) for the experiment. [Note: This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility, operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.] The in situ microwave reactor was modified with a commercial Monowave 300 reactor (Anton Paar). The direct x-ray beam was blocked by a beam stopper with size of 0.3 mm × 0.3 mm, and the scattered x-ray signals were collected by an array of four GE 41RT detector at the frequency of 1 pattern per minute. Transmission electron microscope (JEOL 2100F) was used to characterize morphology, size, and size distribution of the as-synthesized Ag nanoparticles.



Figure S1. Scheme illustration of the in situ experiment setup.

Section II: Full-version LSW model of growing colloidal Ag nanoparticle

In the formation of Ag nanoparticles from reduction of AgNO₃, the reduction of Ag(I) for a period of time at an appropriate temperature accumulates a high enough concentration (i.e., high supersaturation) of Ag⁰ atoms to trigger a spontaneous formation of solid Ag nuclei. In general, the growth of nuclei quickly consumes Ag⁰ atoms to lower its supersaturation, resulting in a cease of nucleation that requires a high supersaturation of Ag⁰ atoms. Once the stable nuclei are formed in the solution, heterogeneous reduction of precursor Ag(I) species on the surfaces of nuclei becomes favorable to enlarge the nuclei into nanoparticles with desirable sizes because this growth process is thermodynamically favorable. Therefore, the instantaneous nucleation and evolutionary growth steps are well separated to determine the synthesis of colloidal nanoparticles.

The heterogeneous solid/liquid reduction reaction represents one of the crucial step to determine the growth kinetics of colloidal Ag nanoparticles. Because the precursor Ag(I) species is supplied in solution phase and the reduction reaction occurs on the surface of growing Ag nanoparticles, diffusion of the precursor Ag(I) species to the nanoparticle surface is also important to determine the growth kinetics of Ag nanoparticles. The LSW model represents the well-accepted model describing growth kinetics of nanoparticles, i.e., enlargement rate of the nanoparticles as a function of growth time. In the LSW model, the consumption rate of the Ag(I) precursors (J_{rxn}) is equal to the supply rate of diffusion flux (J_{diff}), which supports the growth of Ag nanoparticles (Figure 1a, main text). The corresponding enlargement rate of growing Ag nanoparticles will be

$$\frac{4\pi r^2}{V_m} \cdot \frac{dr}{dt} = J_{rxn} = J_{diff}$$
(S1)

in which V_m , t, and r are the molar volume of Ag metal, the growth time, and radius of the growing Ag nanoparticle at time t, respectively. If the surface reduction of precursor Ag(I) species is assumed to be first order with respect to both the precursor Ag(I) species and the surface of growing Ag nanoparticle, the consumption rate J_{rxn} of a spherical nanoparticle can be represented by:

$$J_{rxn} = k \cdot 4\pi r^2 \cdot (C_i - C_r)$$
(S2)

 C_i represents the concentration of the precursor Ag(I) species at the imaginary solid/liquid interface *i* (the dashed circle in Figure 1a). C_r is the concentration of the precursor Ag(I) species at the solid surface of the nanoparticle, which is equal to the solubility of Ag atoms and is negligibly small

under the reaction conditions. k represents the heterogeneous reaction rate constant of reducing the precursor Ag(I) species on the Ag nanoparticle surface. Meanwhile, the diffusion of Ag(I) precursor is assumed to follow the Fick's first law that can described by:

$$J_{diff} = \frac{4\pi Dr(r+\delta)}{\delta} (C_b - C_i) \approx 4\pi Dr(C_b - C_i), \text{ when } \delta \gg r$$
(S3)

in which D, δ , and C_b stand for diffusion coefficient, diffusion layer thickness, and bulk solution concentration of Ag(I) precursor species. A general description of the enlargement rate of a single Ag nanoparticle can be expressed by combining eq. (S1-S3):

$$\frac{dr}{dt} = \frac{kD}{kr+D} V_m (C_b - C_r) \approx \frac{kD}{kr+D} V_m C_b, \text{ when } C_b \gg C_r$$
(S4)

The reduction of Ag(I) precursor to grow Ag nanoparticles consumes the Ag(I) precursor in the bulk solution, leading to a monotonous decrease of C_b :

$$C_b = C_0 - \frac{V_{Ag, total}}{V_m \cdot V_s} \tag{S5}$$

where C_0 is the initial concentration of the Ag(I) precursor (i.e., the concentration of AgNO₃), V_s is the volume of the reaction solution, and $V_{Ag,total}$ is the total volume of the solid Ag nanoparticles. It is reasonable to assume that the number of the Ag nanoparticles remains constant as N_0 during the nanoparticle growth after the nucleation, since the burst nucleation stops immediately after the supersaturation level of the solution decreases significantly. Therefore, when Ag nanoparticles in a reaction system enlarges to a radius of r, the concentration of the Ag(I) precursor remaining in bulk solution (C_b) becomes:

$$C_b = C_0 - \frac{N_0 - 4}{V_m \cdot V_s 3} \pi r^3$$
(S6)

Therefore, eq. (S4) can be further reduced to:

$$\frac{dr}{dt} = \frac{kD}{kr+D} V_m \left[C_0 - \frac{4N_0\pi}{3V_m \cdot V_s} r^3 \right] = \frac{kD}{kr+D} \left(a - N_0 \cdot b \cdot r^3 \right)$$
(S7)

in which $a = V_m \cdot C_0$ and $b = \overline{3V_s}$. The constant *a* and *b* can be calculated using V_m of 10.3 cm³ mol⁻¹ and the values of C_0 and V_s for a synthesis solution. This autonomous ordinary differential equation describes the growth rate (dr/dt) as a function of the radius of an individual nanoparticle (*r*). If the ensemble of nanoparticles follows a size distribution that a total number (N_0) of nanoparticles have a volume-weighted average size of \bar{r} :

$$\bar{r} = \left(\frac{3 \, V_{Ag, \, tot}}{4\pi \, N_0}\right)^{\frac{1}{3}} \tag{S8}$$

Eq. (S7) can be rewritten as the change rate of total Ag particle volume $(dV_{Ag,tot}/dt)$ as a function of the Ag particle volume by substituting *r* with $V_{Ag,tot}$. Eq. (S7) is so-called the "full-version" LSV growth model because it includes contributions of both diffusion and surface reaction.

Section III: Data processing and simulated annealing fitting of experimental data

Data pretreatment. The experimental data of growing colloidal Ag nanoparticles was adopted from our previous work.¹ The 2D pattern recorded by the x-ray detector was calibrated with a standard LaB₆ sample and unreacted reaction mixtures. The 2D ring pattern was then reduced to 1D HEXRD pattern using Fit2D software. The as-synthesized Ag particles exhibited HEXRD patterns of a typical face-centered cubic (*fcc*) lattice, showing (111), (200), and (220) peaks at 4.3°, 5.0°, and 7.0° (**Figure S2**a). Because of the high crystallinity of the Ag nanoparticles, the peak area of HEXRD patterns is proportional to the amount (or volume) of the Ag nanoparticles, which can be determined by referencing with the HEXRD pattern of Ag nanoparticles formed from a complete reduction of the Ag(I) precursor. The (111) peak area integrated from 4.2° to 4.4° is used to calculate the total amount (or particle volume) of growing Ag nanoparticles (Figure S2b). Complete reduction of 0.1 M AgNO₃ in 6-mL solution formed 6.18 mm³ of Ag at the longest reaction time (i.e., in the plateau region in Figure S2c). The time-dependent data points are converted to the total volumes (V_{tot} /mm³), which were fitting with the simulated annealing program. The time-dependent peak area of (200) peaks are also presented for comparison (Figure S2d).



Figure S2. (a) HEXRD patterns of the reaction solution for synthesizing colloidal Ag nanoparticles at 140 °C in the in situ microwave reactor. The time interval for recording the HEXRD patterns was 1 minute. (b) Blowup of the (111) peaks. (c) Integrated (111) peak areas of the syntheses at different temperatures: 130 °C (blue, \blacksquare), 140 °C (green, \bullet), 160 °C (orange, \bullet), and 180 °C (red, \blacktriangle). The time-dependent peak areas were converted to the total volume of growing Ag nanoparticles ($V_{Ag,tot}$, right axis). (d) Integrated (200) peak areas of the syntheses at different temperatures.

It is worthy of pointing out that the sensitivity of the in-situ HEXRD is not high enough to probe the formation of Ag nuclei and their growth at the very early stage when the total volume of the growing Ag nanoparticles is less than ~1% of V_{max} (or <~0.06 mm³). The Ag nanoparticles formed at the nucleation stage and early growth stage ($t_{exp} < 10 \text{ min}$) are small in size and lack of long-range order of crystallinity to exhibit HEXRD patterns with a reasonable signal-to-noise ratio. The lateral dimensions of Ag nanoparticles along Ag[111] and Ag[200] directions can also be estimated from the full width at half maximum (FWHM) of the corresponding peaks of in situ HEXRD patterns using Scherrer equation. Although the lateral dimension along Ag[111] expands slightly faster than that along Ag[200] at the early stage, the expansion of Ag nanoparticles along both directions shows similar sigmoidal profiles (Figure S3c-d), indicating a general isotropic growth throughout the entire synthesis. Therefore, the maximum lateral dimensions at the longest reaction time can be used as the diameters of the nanoparticles to calculate N_0 according to $N_0 = V/(\frac{4}{3}\pi r^3)$. The time-dependent evolution of the total volume of Ag nanoparticles ($V_{tot}(t)$) using $V_{tot}(t) = \frac{4}{3}\pi r^3(t) \cdot N_0$

Initial estimation of k and D using the extreme-condition model. A proper initial guess of the values of *k* and *D* can significantly improve the performance of the simulated annealing algorithm and increase the efficiency to reach a converged result since it helps narrow the searching zone to a reasonable magnitude. The extreme-condition model from our previous work² was applied to obtain the initial guess of the values of *k* and *D* from a growth curve. The initial guess of the *k* value can be obtained from the slope of the $V_{tot}^{1/3}$ vs *t* plot at the very beginning stage (**Figure S3**a):

$$\frac{d(V_{tot}^{1/3})}{dt}\Big|_{\bar{r} \ll \bar{r}_{max}} = \left(\frac{4\pi N_0}{3}\right)^{1/3} ka$$
(S9)

and the D value can be obtained from the slope of the $\ln(V_{tot,max}^{1/3} - V_{tot}^{1/3})$ vs t plot at the very late stage (Figure S3b):

$$\frac{d\left[\ln\left(V_{tot,max}^{-1/3} - V_{tot}^{1/3}\right)\right]}{dt}\Big|_{\bar{r}\to\bar{r}_{max}} = -3\left(a^2 \cdot b \cdot N_0\right)^{\frac{1}{3}} \cdot \frac{kD}{k\bar{r}_{max} + D}$$
(S10)

4π

a and *b* are constants that only related to the synthesis condition, i.e., $a = V_m \cdot C_0$ and $b = \frac{4\pi}{3V_s}$. The initial action of the synthesis condition, i.e., $a = V_m \cdot C_0$ and $b = \frac{4\pi}{3V_s}$. The initial estimations of k and D for the synthesis at different temperatures are listed in **Table S1**. It is worthy of pointing out that the extreme condition model focusing only on the two special stages is not able to determine the accurate values of k and D, particularly when the temporal resolution of data collection is low and the data value variation rate is small. Despite of the challenge, the values of k and D can be used as the starting point for the simulated annealing fitting that relies on all data points of the entire growth.



Figure S3. (a) The $V^{1/3} \sim t$ plot of the data shown in Fig. S2c for determining the initial guess of k by using the slope of linear fitting of data points at the very early growth stage according to eq. (S9). (b) The $\ln(V^{1/3}_{max})$ $-V^{1/3}$) ~ t plot of the data shown in Fig. S2c for determining the initial guess of D by using the slope of linear fitting of data points at the very late growth stage according to eq. (S10).

Temp.	$2^{\overline{r}_{max^*}}$	N_0	k	D	η^{***}
/°C	/nm	/1012	$/10^{-7} \mathrm{m} \cdot \mathrm{s}^{-1}$	$/10^{-14} m^2 \cdot s^{-1}$	/mPa·s
130	60	11	0.46	N/A**	1.99
140	103	11	0.78	0.15	1.79
160	116	7.5	2.7	3.92	1.44
180	143	4.0	6.75	21.7	1.21

Table S1. The initial estimation of k and D values using the extreme-condition model for the synthesis atdifferent temperatures.

 $([AgNO_3] = 0.10M [PVP] = 0.15M V_s = 6.0 mL)$

*Calculated from the statistic average size measured from TEM images

No available data for the very-late stage, using estimated $D = 0.07 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ as initial guess. *The viscosity of PVP-K30/EG solution are calculated from the Fikentscher's equation³: $\frac{\log (\eta_{rel})}{c} = \frac{75K_0^2}{1 + 1.5K_0c} + K_0$

4th order Runge-Kutta method. Upon the implementation of the values of (k, D) pair, the nanoparticle growth trajectory $(r(t) \sim t)$ can be calculated according to the full version LSW model (eq. S7). In order to numerically solve this autonomous ordinary differential equation (dr = r'(r, t))

 $\frac{dr}{dt} = r'(r,t)$), the classic 4th order Runge-Kutta method (RK4) with an initial condition $r(t_0)>0$ was applied. In RK4 method, once a point on the growth trajectory curve ($r(t_0) = r_0$) was given, the value on one stepwise after this point ($r(t_0+h)$) can be approximately represented by:

$$r(t_0 + h) = r_0 + \frac{1}{6}h(k_1 + 2k_2 + 2k_3 + k_4)$$
(S11)

where $k_1 \sim k_4$ are the slopes at the beginning, midpoints, and end point of this step:

$$\begin{pmatrix}
k_{1} = r'(r_{0},t_{0}) \\
k_{2} = r'(r_{0} + \frac{hk_{1}}{2},t_{0} + \frac{h}{2}) \\
k_{3} = r'\left(r_{0} + \frac{hk_{2}}{2},t_{0} + \frac{h}{2}\right) \\
k_{4} = r'(r_{0} + hk_{3},t_{0} + h)
\end{cases}$$
(S12)

By repeating the RK4 method step after step, a series of points of r(t+nh) (n = 1, 2, 3, ...) can be numerically estimated. When the length of the step *h* is small enough, the numerical estimation of

r(t) curve converges to the analytical solution of the differential equation $(\frac{dr}{dt} = r'(r,t))$. The RK4 method can also be used backwards when the step length *h* is negative.

In this work, the starting point $r(t_0)$ was set to the midpoint of the growth curve where the first derivative (i.e., dV_{tot}/dt) reaches the maximum to minimize the relative error in determining the slope. The points before the midpoint were calculated by RK4 using $h = -1 \times 10^{-4}$ min and the points after that was calculated by using $h = 1 \times 10^{-4}$ min, which was much smaller than the temporal density of the experimental data points (1 point/min). The estimated r(t) profile was converted to

the total volume
$$(V_{\text{tot}}(t))$$
 profile using $V_{tot} = \frac{4}{3}N_0\pi r(t)^3$

Simulated annealing algorithm. Once the value of a (k, D) pair is available, the data points estimated by RK4 (as V_{fit}) at the experimental time series (i.e., t=1, 2, 3, ... min) were picked out to calculate the sum of squared residuals (SSR) with respect to the experimental data series (V_{exp}).

$$SSR = \sum_{i} |V_{fit}(t_{i}) - V_{exp}(t_{i})|^{2}$$
(S13)

A large *SSR* suggests a low-fidelity fitting of the input (k, D) pair while a small *SSR* indicates an appropriate fitting. Therefore, one can try as many (k, D) pairs as possible to find the best solution to fit the experimental data (so called Monte-Carlo method). However, such a completely random manner makes the computation process to be costly. The algorithm is improved by applying simulated annealing strategy, where the possibility of acceptance (P) of the new (k, D) pair is determined by the Metropolis's rule. A smaller *SSR* will be accepted immediately (P=1), and a larger *SSR* will be accepted conditionally:

$$P(k, D) = \begin{cases} 1, SSR_{n+1} < SSR\\ \exp\left(-\frac{|SSR_{n+1} - SSR|}{R\tau}\right), SSR_{n+1} \ge SSR \end{cases}$$
(S14)

R is a constant that only related to the efficiency of the algorithm and τ is the current "temperature" of the simulated annealing process that decreases after each iteration of searching. In our C-program, the simulated annealing algorithm is realized by the following iterations (described in plain text, note that all physical values including *k* and *D* are normalized to cancel the units to adapt the programming language):

- 1. $\tau = 100$, R=0.01, $(k, D) = (k_0, D_0)$ (initial guess evaluated from the extreme-condition model).
- 2. Calculate SSR using the RK4 method with the current (k, D) values.
- 3. Randomly pick a new (k, D) pair within the range of $k_{n+1} \in [k \frac{\tau}{2}, k + \frac{\tau}{2}]$, $D_{n+1} \in [D - \frac{\tau}{2}, D + \frac{\tau}{2}]$.
- 4. Calculate SSR_{n+1} using the RK4 method with the current $(k, D)_{n+1}$ values.
- 5. Generate a random number *i* between 0 and 1.
- 6. Calculate the possibility of acceptance P(k, D)
 - If $P(k, D) \ge i$ (accepted)
 - i. Save $(k, D)_{n+1}$ and SSR_{n+1} in memory as (k, D) and SSR, respectively.
 - ii. Cool down the "temperature" $\tau = 0.99\tau$ (0.99 is the cooling rate)
 - iii. Go to step 3.
 - If P(k, D) < i (rejected)
 - i. Keep the old (k, D) and SSR in memory
 - ii. Go to step 3.
- 7. Repeat steps 3-6 until $\tau < 0.1$
- 8. Print the (k, D), SSR, and the fitted $V_{fit}(t)$ in memory.

The computational parameters ($\tau_{max} = 100$, $\tau_{min} = 0.1$, *R*=0.01, and the cooling rate 0.99) have already been optimized to achieve the convergency as well as to adapt the computational environments. Using these parameters, it only takes approximately 1 hour to run 100 independent

iterations on a laptop equipped with an Intel® CoreTM i5-7200U processor. The computation can be accelerated by choosing a lower threshold of convergency (for example, a higher τ_{min} or a more rapid cooling rate) or coarsening the RK4 step length at the cost of the accuracy and stability of the output results or vice versa. However, due to the dice-rolling feature of the algorithm, the improvement on the output results, in a statistical manner, is not significantly affected by these parameters. A sample code of the C program attached with a brief instruction document can be found at Github: <u>https://github.com/wsy94/NanoGK</u>



Figure S4. Flow chart of the simulated annealing algorithm. Insert: The maximum point at the first derivative function is chosen as the center for the two-way RK4 method.



Figure S5. The optimized (*k*, *D*) pairs determined from the simulated annealing fitting of the growth kinetics of colloidal Ag nanoparticles measured from the syntheses at different temperatures: (a) 130° C, (b) 140° C, (c) 160° C, and (d) 180° C. The concentration of AgNO₃ was 0.1 M and the concentration of PVP in terms of repeat unit was 0.15 M. The colors of dots correspond to the *SSRs* calculated between the experimental data and the fitting data.

Temp.	triala	k	$\sigma(k)$	D	$\sigma(D)$
/°C	ulais	$/10^{-7} \text{ m} \cdot \text{s}^{-1}$	$/10^{-7} \text{ m} \cdot \text{s}^{-1}$	$/10^{-14} m^2 \cdot s^{-1}$	$/10^{-14} m^2 \cdot s^{-1}$
130	100	0.22	0.002	1.19	0.37
140	100	0.76	0.011	1.83	0.32
160	100	2.87	0.052	8.13	2.24
180	200	9.33	0.313	15.7	4.2



Figure S6. The optimized (k, D) pairs determined from the simulated annealing fitting of the growth kinetics of colloidal Ag nanoparticles measured from the syntheses at different AgNO₃ concentrations: (a) 0.05 M, (b) 0.10 M, and (c) 0.15 M. The temperature was 160 °C and the concentration of PVP in terms of repeat unit was 0.15 M. The colors of dots correspond to the *SSRs* calculated between the experimental data and the fitting data.

Table S3. Analysis on the	output (k, D) values at	different AgNO ₃ concentrations*
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[Ag] /M	2 ^r max* /nm	N ₀ /10 ¹²	trials	<i>k</i> /10 ⁻⁷ m·s ⁻¹	$\sigma(k)$ /10 ⁻⁷ m·s ⁻¹	D/10 ⁻¹⁴ m ² ·s ⁻¹	$\sigma(D)$ /10 ⁻¹⁴ m ² ·s ⁻¹
0.05	110	5.54	200	6.21	0.31	10.65	3.04
0.10	116	9.45	100	2.85	0.09	9.68	2.75
0.15	123	11.89	100	2.12	0.02	10.23	1.93

*Statistics are based on the top 10% best results. Conditions: T=160 °C, [PVP] = 0.15 M, $V_s = 6.0$ mL.

Section IV: Density functional theory (DFT) calculations on Ag-PVP complexes

Density functional theory (DFT) calculations. In the Ag-PVP system, the complex species of an Ag⁰ or Ag⁺ center coordinated with 1-2 of the repeating units (i.e., vinylpyrrolidone, VP) are used as the simplified models to reduce the computation time. The possible electron donor atom in VP can be the nitrogen atom and/or the oxygen atom. Both of the two cases are calculated. The calculations are all conducted at the ground state (i.e., the lowest possible multiplicity). The initial iteration of the geometry optimization is first optimized by molecular dynamics using MM3 method and then by B3LYP method^{4,5} to achieve a higher-level accuracy. The standard relativistic effective core potential LanL2DZ basis set⁶ is used for the metal center (i.e., Ag) involved in the calculation, while the other light atoms (H, C, N, O) of VP are calculated using the 6-31G(d) basis set.⁷ The geometry and the B3LYP level energy of the last iteration of the geometry optimizations are adopted for discussion in this work. The calculation by B3LYP method using cc-pVDZ basis set⁸ (on light atoms) and the calculation by MP2 method⁹ at 6-31G(d) (on light atoms) are also performed for comparison. If the geometry optimization is not converging, for example, in calculating the transient states, single point energy calculations using the same geometry as either the non-ionic or ionic form are conducted. All of the calculations are performed on the WebMO 12.0 (WebMO, LLC) interface, which runs Gaussian 09TM (Gaussian, Inc.).

In a real synthesis of colloidal Ag nanoparticles, EG plays the roles of both solvent and reductant. In order to study the solvent effect, we consider the implicit model where the solvent molecules are treated as a polarizable continuous electric field.

The interaction between the metal center and the ligand can be described by the bond formation energy (E_{BF}) , which is defined as the energy difference between the metal-ligand complex $(E(M - L_n))$ and the sum of the energies of isolated metal center E(M) and ligand molecules E(L):

$$E_{BF} = E(M - L_n) - [E(M) - nE(L)]$$
(S15)

where n is the number of ligand molecules that form coordination bond with the metal center. The reducibility of the metal ions or metal ion complex from the oxidation state to the corresponding reduction state are described by the first ionization energy, which is defined by the energy difference between the two states:

$$E_{IE} = E(M - L_n^+) - E(M - L_n)$$
(S16)

It is worth pointing out that E_{IE} is not same as the reduction potential due to the solvent effect. The calculations considering the solvent effect are also performed and discussed in this work, where the solvent (i.e., ethylene glycol) is treated implicitly as a polarizable continuous electric field.

Results and discussion from DFT calculations. In a synthesis of colloidal Ag nanoparticles, PVP is considered as a surfactant ligand that plays an important role of stabilizing the surface of nanoparticles and preventing aggregation of nanoparticles. PVP can also form complexes with metal precursor ions to influence the reaction kinetics.¹⁰ A monomeric unit of PVP (VP) consists of a vinyl group and a 2-pyrrolidone ring containing a nitrogen atom and an oxygen atom as potential electron donors to the metal. To figure out the most stable coordination state in each case, we optimized the geometry and calculated the $E_{\rm BF}$ using VP as a model of the repeating unit. It is worthy to point out that the vinyl group in the monomer with two sp^2 C is substituted by the ethyl group with two sp^3 C, which has the closest structure to the polymerized hydrocarbon chain. The calculation results suggest that the coordination of Ag⁺ to the oxygen atom (denoted by Ag⁺-O-VP) of VP has the lowest $E_{\rm BF}$ (-38.3 kJ/mol) and the coordination of Ag⁺ to the nitrogen atom (Ag⁺-N-VP) has a less negative E_{BF} (-2.97 kJ/mol). Therefore, when AgNO₃ is dissolved in a EG solution that contains PVP, the free-standing Ag⁺ ions tend to coordinate with the O atoms of the PVP ligand, forming a stable complex and lowering the actual concentration of ligand-free Ag⁺. The Mulliken partial charge on Ag⁺-O-VP is calculated to be +0.773, smaller than that of a freestanding Ag⁺ cation (i.e., +1). The drop of the partial charge indicates that the electron donation of O atom enriches the electron density on Ag⁺ and makes the reduction easier. The energy difference between the ionized Ag⁺-O-VP and non-ionized Ag⁰-O-VP is also smaller than that between Ag⁺ and Ag⁰, which agrees with the conclusion that the reduction of Ag⁺-PVP costs less energy.

Once Ag^+ is reduced to Ag^0 , the coordination bond between Ag and VP ligand is weakened in both the O bonded and N bonded configurations. The E_{BF} of Ag^0 -O-VP is calculated to be 6.18 kJ/mol, as the distance between the Ag^0 atom and the electron donor (O atom) in the optimized geometries of Ag^0 -O-VP is enlarged to 2.581 Å. The positive E_{BF} and the elongated coordination bond suggest that the PVP molecules is likely to interact with the reduced Ag^0 through physical adsorption rather than chemical bonding, enabling the continuous surface growth of Ag nanoparticles. In a brief summary, the DFT calculations predict that the oxygen atom in the VP monomer is the most possible electron donor atom to coordinate with the Ag center. The conclusion agrees well with the experimental observation in the FTIR study¹¹ and the molecular dynamics simulation¹² reported in literature.



Figure S7. Optimized geometries of different coordination states: (a) Ag⁺-N-VP, (b) Ag⁺-O-VP, and (c) Ag⁰-N-VP.

Having determined that the oxygen atom is the electron donor atom in a repeating unit of PVP, we step forward to study the case where Ag^0 or Ag^+ is coordinated with two repeating units (VP)₂, The calculation results are presented in Table S4 and compared in Figure S8. The geometry optimization of the two VP molecules results in a conformation where the two VP molecules are coordinates with the center Ag atom/ion in a linear geometry using the O atoms. The Ag⁺-O bond length is 2.17Å in Ag⁺-(O-VP)₂. The E_{BF} of the second Ag⁺-(O-VP) bond is calculated as -60.6 kJ/mol, even more exergonic than forming the single-coordination complex Ag⁺-(O-VP). The geometry optimization of the non-ionic Ag⁰-(O-VP)₂ complex shows a longer Ag-O bond length of 2.68Å, indicating a weaker interaction between the atomic Ag⁰ and the electron donors. The E_{BF} is 84.1 kJ/mol, indicating that forming the second coordination bond to Ag⁰ atom is unlikely.

Object	Units	LAND2DZ	B3LYP/6-31G(d)	B3LYP/cc-pVDZ	MP2/6-31G(d)
Ag^0	Hartree	-145.7611714			-144.9520879
Ag^+	Hartree	-145.6284244			-144.8618252
$E_{\mathrm{IE.0}}$	Hartree	0.132747			0.090263
	kJ/mol	345.1421			234.6830
VP_1	Hartree		-365.2683355	-365.403344767	-364.0688884
Ag ⁰ -VP	Hartree		-511.027129	-511.164864	-509.0125786
$E_{ m BF}$	Hartree		0.002378	-0.00035	0.008397638
	kJ/mol		6.1827	-0.90411	21.8339
Ag ⁺ -VP	Hartree		-510.9114801	-511.0472711	-508.9314677
E_{BF}	Hartree		-0.01472	-0.0155	-0.000754119
	kJ/mol		-38.2722	-40.3049	-1.96071
$E_{\mathrm{IE.1}}$	Hartree		0.115649	0.117593	0.081111
	kJ/mol		300.6872	305.7413	210.8884
Ag ⁰ -VP ₂	Hartree		-876.2631195	-876.5406506	-873.0372545
$E_{\mathrm{BF.2}}$	Hartree		0.032345	0.027558	0.044212
	kJ/mol		84.09702	71.65121	114.95232
Ag^+-VP_2	Hartree		-876.203115809	-876.4745159	-873.0091584
$E_{\rm BF.2}$	Hartree		-0.0233	-0.0239	-0.008802
	kJ/mol		-60.5806	-62.1399	-22.8861
$E_{\mathrm{IE.2}}$	Hartree		0.060004	0.066135	0.028096
	kJ/mol		156.0096	171.9502	73.0500

Table S4. DFT calculation results of various Ag-VP complexes using different methods.

The calculations based on B3LYP method using cc-pVDZ basis set (on light atoms) and the calculations based on MP2 method at 6-31G(d) (on light atoms) are also performed for comparison. The cc-pVDZ with a more complex basis set (compared to 6-31G(d)) has a higher accuracy but is more computationally expensive. The ground state energies, the bond formation energies (E_{BF}), and the ionization energies (E_{IE}) of each coordination state of Ag-VP complexes do not have a significant difference. The calculations from MP2, based on the many-body

perturbation theories, are much less accurate, with only the consistence on the orders of energies of different coordination states.



Figure S8. Energy diagram of various Ag-VP complexes calculated by DFT. The energy of freestanding Ag⁺ cation is set as the reference zero.

The difference between the theoretical predictions and the experiment results can be attributed to several aspects. First, the implicit model does not include a sufficient amount of individual solvent molecules to mimic the actual condition, resulting in the deviation caused by missing the possible strong chemical interaction between the metal and solvent molecules. Second, the folding configuration of polymeric PVP and the partially charged double layer near the surface of the nanoparticles may cause the electronic structure of the metal complexes to be different from the simplified model between Ag and monomeric VP.

In conclusion, the actual Ag precursor species involved in the surface reduction reaction is Ag- $(O-VP)_n$ complex rather than all Ag(I) species that is used in the simulated annealing fitting. The difference between in the actual concentration of [Ag- $(O-VP)_n$] and the initial [AgNO₃] calculated

from the total $AgNO_3$ used for solution leads to the fitted *k* decreases as the amount of added $AgNO_3$ increases even at the same temperature.

Attachment: A sample input.com file for Gaussian 09 calculation of Ag⁺-(O-VP)₁

#N B3LYP/GEN opt SCRF=(PCM,Solvent=1,2-EthaneDiol) pseudo=read C6H110NAg 1 1 С C 1 B1 N 1 B2 2 A1 C 1 B3 2 A2 3 D1 C 1 B4 2 A3 3 D2 H 1 B5 2 A4 3 D3 H 1 B6 2 A5 3 D4 0 1 B7 2 A6 3 D5 Ag 1 B8 2 A7 3 D6 C 1 B9 2 A8 3 D7 C 1 B10 2 A9 3 D8 H 1 B11 2 A10 3 D9 H 1 B12 2 A11 3 D10 H 1 B13 2 A12 3 D11 H 1 B14 2 A13 3 D12 H 1 B15 2 A14 3 D13 H 1 B16 2 A15 3 D14 H 1 B17 2 A16 3 D15 H 1 B18 2 A17 3 D16 H 1 B19 2 A18 3 D17 B1 1.552505133 B2 2.392297513 B3 2.424886213 B4 1.549567337 B5 2.215055929 B6 2.227349722

B7 3.653601800
B8 5.793730781
B9 3.803138897
B10 4.481972894
B11 4.276944555
B12 5.526780967
B13 4.607342665
B14 4.153276921
B15 4.472971499
B16 2.217215908
B17 2.216749595
B18 1.092664195
B19 1.094558156
A1 37.17310470
A2 69.18803169
A3 104.3598295
A4 105.6116468
A5 124.0832490
A6 76.06952264
A7 68.31231653
A8 30.06414161
A9 35.09267052
A10 33.56452468
A11 31.51183987
A12 48.84051571
A13 17.61456029
A14 40.37504671
A15 27.08266753
A16 27.24902196
A17 111.5598494
A18 110.0068537
D1 7.876505743
D2 21.32231062
D3 49.52597281
D4 1.406312525
D5 6.833842453
D6 3.877243279

D7 -7.080223208 D8 -42.17335480 D9 -67.22589157 D10 -39.63171417 D11 -41.19945684 D12 14.57375060 D13 3.898030214 D14 -119.2412109 D15 117.9475921 D16 143.0927360 D17 -96.83604817 Ag Ø LANL2DZ **** СНИОО 6-31G(d) **** Ag Ø

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LANL2DZ

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S23

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