

SUPPORTING INFORMATION

Silver Nanoparticles Synthesized by Microwave Heating: A Kinetic and Mechanistic Re-Analysis and Re-Interpretation

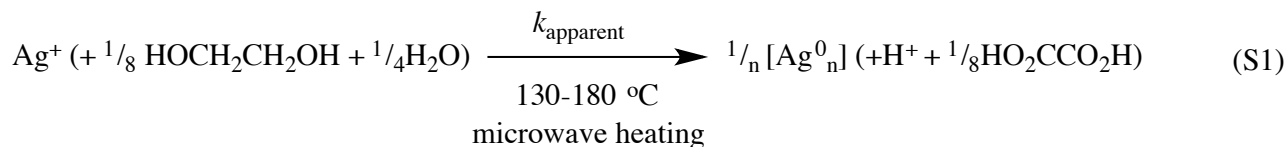
Saim Özkar,^a Richard G. Finke^{*b}

^a Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey

^b Department of Chemistry, Colorado State University, Fort Collins, CO 80523 USA

S1. Derivation of Kinetic Equations Employed for Curve Fitting

The balanced reaction, eq (7) of the main text, rewritten in a simplified form useful for the kinetics derivation is given in eq (S1):



What is actually monitored is the peak area in the HEXRD of either the Ag(111) or Ag(200) facets.

What we need is a form of the FW 2-step mechanism in terms of the HEXRD peak area.

The 2-step mechanism is repeated in eqs (S2a)-(S2c) below; the associated integrated $[\text{B}]_t$ and differential $d[\text{B}]/dt$ equations (S3) and (S4) have been derived previously.¹



$$[\text{B}]_t = [\text{A}]_o \left(1 - \frac{k_1 + k_2 [\text{A}]_o}{k_2 [\text{A}]_o + k_1 e^{(k_1 + k_2 [\text{A}]_o)t}} \right) \quad (\text{S3})$$

$$\frac{d[\text{B}]}{dt} = k_1 [\text{A}]_o \cdot e^{(k_1 + k_2 [\text{A}]_o)t} \cdot \left(\frac{k_1 + k_2 [\text{A}]_o}{k_2 [\text{A}]_o + k_1 e^{(k_1 + k_2 [\text{A}]_o)t}} \right)^2 \quad (\text{S4})$$

All these equations are in terms of effective concentration of A and B. Since the 2016 paper reports the HEXRD peak area (= PA) we need to derive the equations in terms of PA. Such a derivation requires the interconversion of peak area and silver metal concentration. Given that XRD PA is proportional to the Ag^0 mass,^{2,3,4} m_{Ag} , and hence to the moles of Ag^0 , equation (S5) results, where M_{Ag} is the molar mass of Ag:

$$\text{PA}_{\text{Ag}} \propto \frac{m_{\text{Ag}}}{M_{\text{Ag}}} \quad (\text{S5})$$

Since the reaction is performed in a constant volume, V, the PA_{Ag} is proportional to the effective molarity of Ag^0 formed, eqs (S6), (S7) and (S8) result, C is a constant.

$$\text{PA}_{\text{Ag}} \propto \frac{m_{\text{Ag}}}{V \cdot M_{\text{Ag}}} \quad (\text{S6})$$

$$PA_{Ag} = C \cdot [Ag^0] = C \cdot [B] \quad (S7)$$

$$[B]_t = \frac{PA_{Ag}}{C} \quad (S8)$$

The constant C can be determined from the known value for limiting conditions. For $[Ag^0] = 0$ at $t = 0$, and for complete conversion of the metal $[Ag^+]_0$ to $[Ag^0]_\infty$ (i.e. for $[Ag^+]_0 = [Ag^0]_\infty$) we also write eq (S9)

$$PA_\infty = C \cdot [Ag^0]_\infty = C \cdot [Ag^+]_0 \quad (S9a)$$

hence, at any time t

$$PA_t = C \cdot [B]_t \quad (S9b)$$

It then follows for metal $[Ag^+]_0 = [A]_0$ (i.e. for $[Ag^+] = [A]$ at all times, t)

$$[A]_0 = [Ag^+]_0 = \frac{PA_\infty}{C} \quad (S10)$$

Looking at eq (S3) for example, (and then analogously for eq (S4)), we can see by substituting eqs (S9b) and (S10) into (S3) that (S11a) results:

$$\frac{PA_t}{C} = \frac{PA_\infty}{C} \left(1 - \frac{k_1 + k_2 \frac{PA_\infty}{C}}{k_2 \frac{PA_\infty}{C} + k_1 e^{(k_1 + k_2 \frac{PA_\infty}{C})t}} \right) \quad (S11a)$$

where $k'_2 = k_2 \frac{1}{C}$ (i.e. $k_2 = Ck'_2$, eq (S11b) results

$$PA_t = PA_\infty \left(1 - \frac{k_1 + k'_2 PA_\infty}{k'_2 PA_\infty + k_1 e^{(k_1 + k'_2 PA_\infty)t}} \right) \quad (S11b)$$

and, again, by definition, $Ck'_2 = k_2$, so that what results from a curve fit is k'_2 (and not k_2).

Note also that eq (S4) analogously becomes eq (S12) and also contains k'_2 not k_2 .

$$\frac{d[PA]}{dt} = k_1 PA_\infty \cdot e^{(k_1 + k'_2 PA_\infty)t} \cdot \left(\frac{k_1 + k'_2 PA_\infty}{k'_2 PA_\infty + k_1 e^{(k_1 + k'_2 PA_\infty)t}} \right)^2 \quad (S12)$$

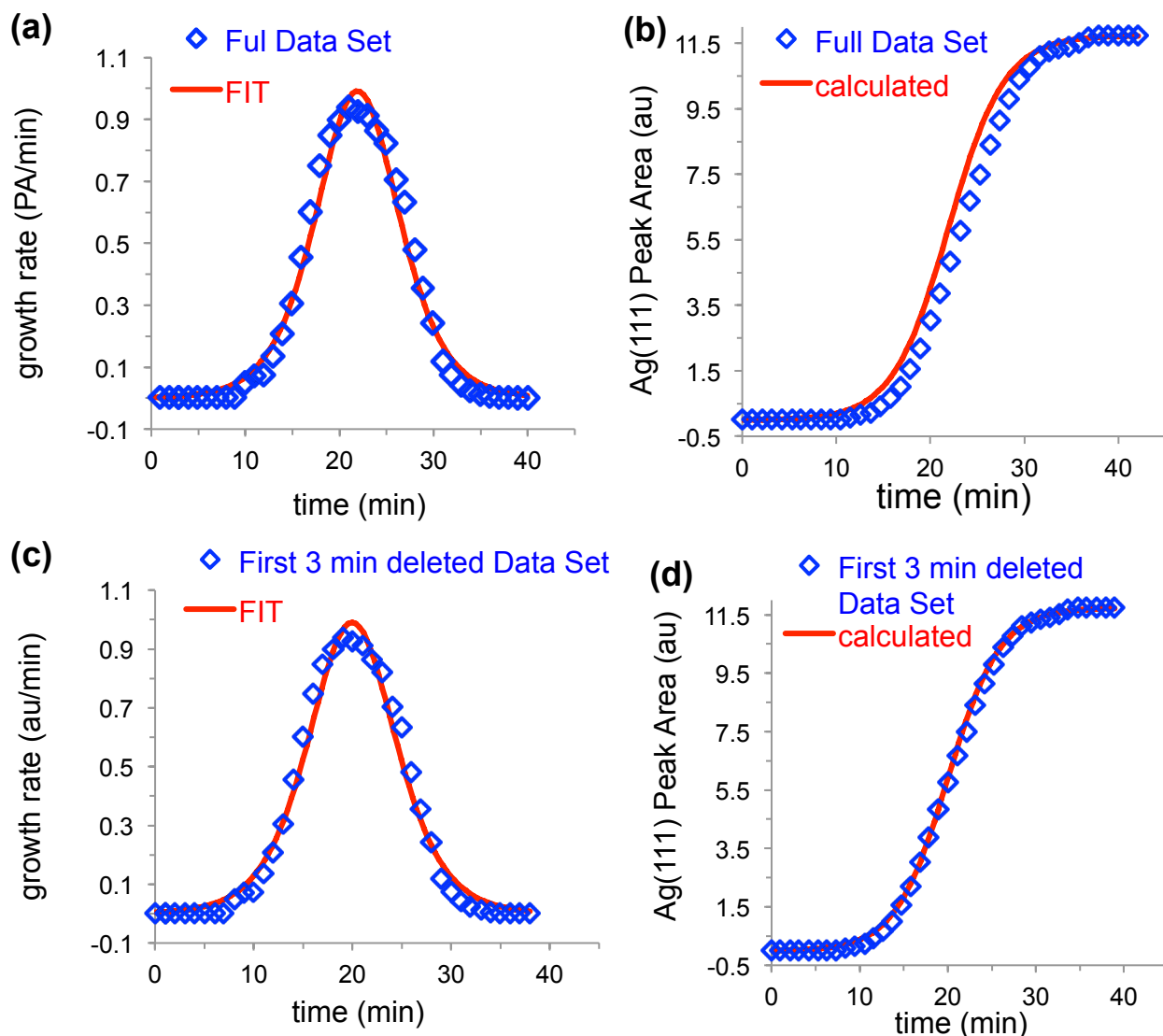


Figure S1. (a) Plot of the experimentally determined growth rate versus time (blue diamonds) given in Figure S4 in the Supporting Information of the 2016 paper⁵ for the $\text{Ag}^+ \rightarrow \text{Ag}^0$ reaction at 140 °C and its fit (red line) to the FW 2-step mechanism⁶ yielding $k_1 = (2.08 \pm 0.29) \times 10^{-4} \text{ min}^{-1}$, $k'_2 = (2.87 \pm 0.06) \times 10^{-2} (\text{a.u.})^{-1} \text{ min}^{-1}$ with a reduced Chi-Sqr = 2.03×10^{-3} , and $R^2 = 0.98317$. (b) Peak area versus time plot (obtained from peak area of Ag(111) reflections in Figure 2A of the 2016 paper⁵) and its simulation using the rate constants obtained in (a) and equation 4 from the main text. (c) The same growth rate versus time plot as in (a) but with the first 3 minutes deleted and its fit to the FW 2-step mechanism⁶ yielding the rate constants $k_1 = (4.00 \pm 0.51) \times 10^{-4} \text{ min}^{-1}$, $k'_2 = (2.87 \pm 0.06) \times 10^{-2} (\text{a.u.})^{-1} \text{ min}^{-1}$ with a reduced Chi-Sqr = 2.14×10^{-3} , and $R^2 = 0.98264$. (d) The same peak area versus time plot as in (b) but with the first 3 minutes deleted and the calculated curve using the rate constants obtained in (c) and equation 4 from the main text.

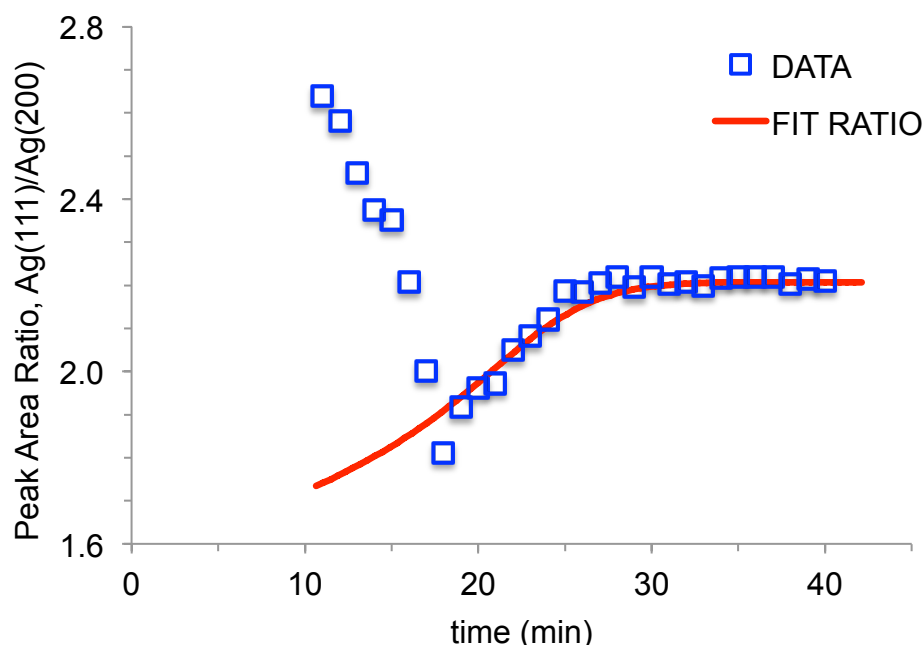


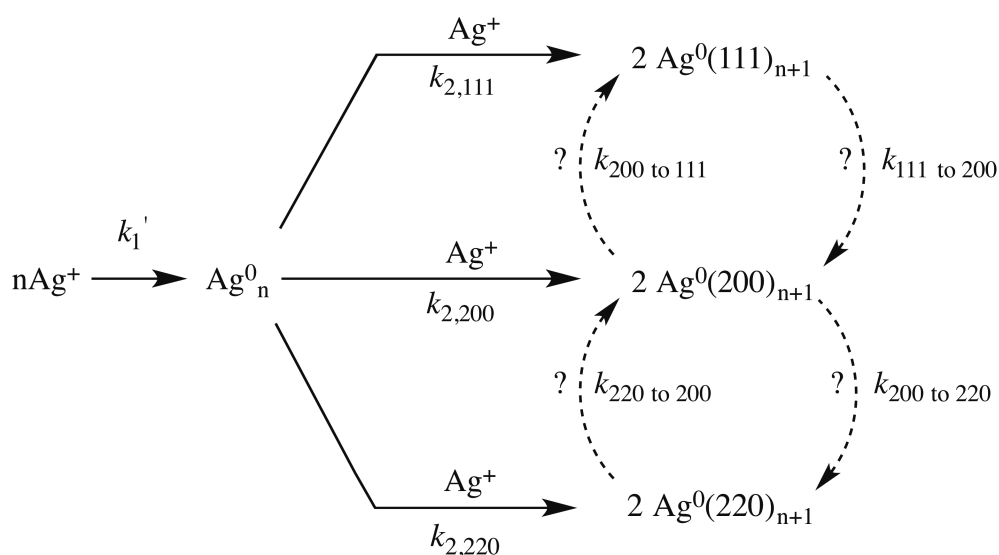
Figure S2. Blue squares show the ratio of experimentally determined ratio of the Ag(111) peak area to the Ag(200) peak area, PA_{111}/PA_{200} , as function of time taken from Figure 2D of the 2016 paper. The red solid curve shows the PA_{111}/PA_{200} ratio calculated as part of the present reanalysis. The separate PA_{111} and then PA_{200} were calculated using eq. 4 in the main text using the rate constants obtained from fits to the FW 2-steps mechanism in Figure 2a and 3, respectively. The PA_{111}/PA_{200} was then calculated vs time and plotted. According to the red line, the initially small PA_{111}/PA_{200} ratio ($=1$ for monoatomic particle) increases towards the steady state value of 2.2 ($=2.3$ for the bulk fcc Ag). Note that there are no error bars on the data (blue squares), since no error estimates are available for this data as part of the 2016 paper and Figure 2D therein.⁵ The small, near zero, hard-to-determine precisely PA_{200} value at short times means that, once those largely unavoidable imprecise values are used in the denominator of the PA_{111}/PA_{200} ratio, this ratio very likely unavoidably has large error bars at low time values, even for the synchrotron-based HEXRD data and in the hands of experts.⁵

Hence and while the data past 18 min is well accounted for, the data below 18 min is far off the indicated data points—although, again, it may well be that the red line is within the true experimental error of the blue squares at shorter times <18 minutes. Note that, unfortunately, whether the red line, or the blue squares, at times <18 minutes are correct is needed to get a better idea of the more intimate mechanism of formation of the Ag(111) and Ag(200) facets—as well as to know if the k_1 and k'_2 rate constants are composites (as we suspect, *vide infra*). If the blue squares below 18 minutes are accurate, then the implication is that a sequential, series reaction of something like $Ag^+ \rightarrow Ag(111) \rightarrow Ag(200)$ is present. Alternatively, the fit by the red line implies parallel reactions, as shown in Scheme S1 below. (There could be a sequential reaction from the Ag(111) to Ag(200) as also shown below just for illustration, as another possibility.) Note that if parallel reactions are present for example, then the rate constants for monitoring any product, for

example *either* the Ag(111) or Ag(200) formation separately, gives, however, the sum of the rate constants that lead to the loss of the reactant (Ag^+ in the present case)—a well known, albeit not necessarily very intuitive, mathematical fact of parallel reaction kinetics.^{7,8} As a consequence, it is not clear whether or not the k_1 and k'_2 rate constants are composites of (in the k'_2 case, for example) possibly $k_{2,111}$, $k_{2,200}$, and $k_{2,220}$ (as these are defined in Scheme S1 below)—although we strongly suspect they are composites of some type.

What is additionally interesting here, but also remains to be understood better, is if the expected different binding constants, for any NO_3^- nanoparticle stabilizer⁹ (recall eq. 1 in the main text) to the two energetically different^{9,10} Ag(111) and Ag(200) facets, have a role in the different growth rates for those facets. In short, much remains to be done to understand the more intimate mechanism of formation of Ag(111) and Ag(200) seen under the interesting reaction conditions in the 2016 study, including obtaining deconvoluted rate constants that refer to underlying, closer-to-elementary, steps.

Scheme S1: One Possible More Detailed Mechanism, Provided Primarily for the Sake of Illustration and to Define Conceivable $k_{2,111}$, $k_{2,200}$, $k_{2,220}$, and $k_{111 \text{ to } 200}$, $k_{200 \text{ to } 111}$, $k_{200 \text{ to } 220}$, and $k_{220 \text{ to } 200}$ Rate Constants (i.e., thereby illustrating how those conceivable underlying steps and their rate constant could be convoluted into^{7,8} the k'_2 measured herein, again all primarily *for the sake of illustration* and to expedite the needed, further research).



$$\left(\text{where } k_1' = \frac{k_1}{n [\text{Ag}^+]^{n-1}} \right)$$

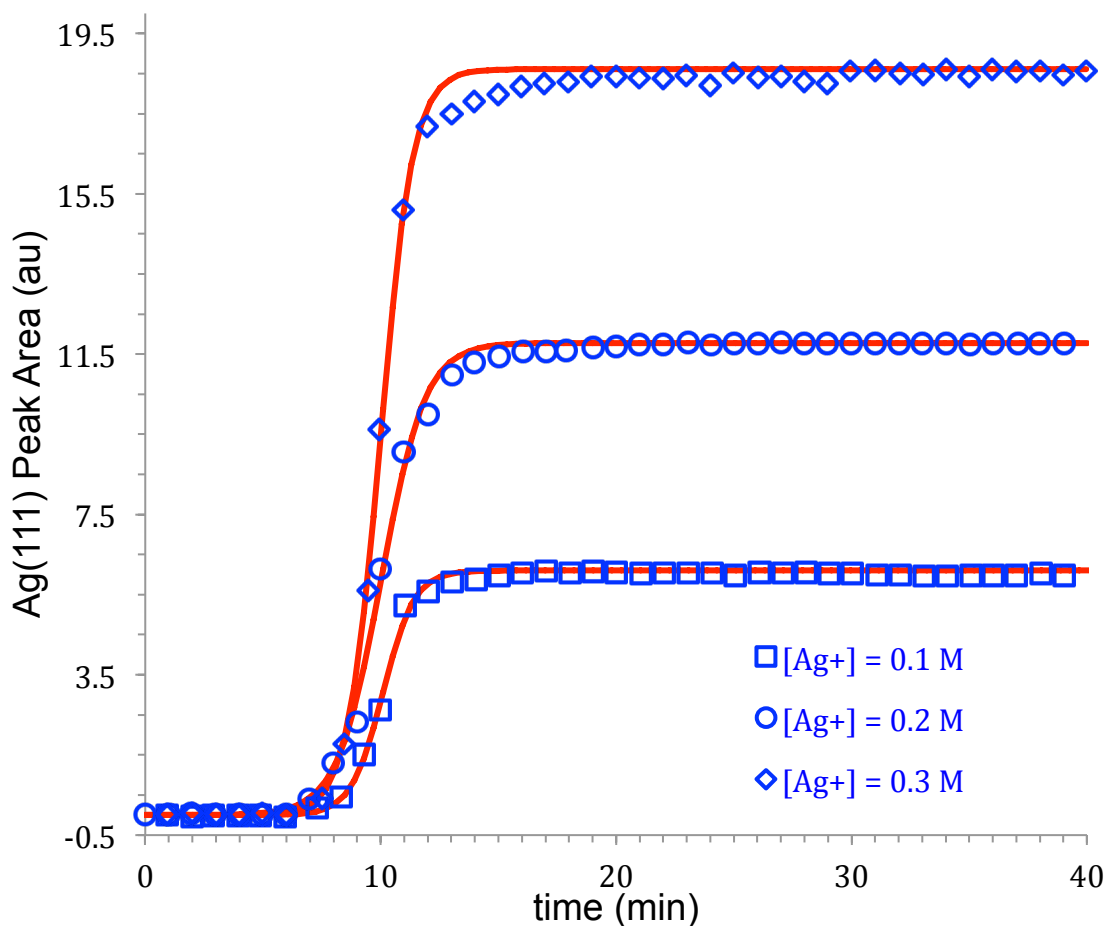


Figure S3. Ag(111) Peak area versus time plot for the formation of Ag(0) nanoparticles from the polyol reduction of silver(I) ions in the indicated different initial concentrations at 140 °C accomplished by microwave heating. The peak area kinetic data were taken from Figure S10 in the Supporting Information of the 2016 paper.⁵ The peak area kinetics data are well-fit by the 2-step FW mechanism,⁶ yielding the rate constants k_1 and k'_2 for the slow, continuous nucleation and autocatalytic surface growth, respectively. Note that the PVP stabilizer concentration was not specified⁵ for these particular experiments.

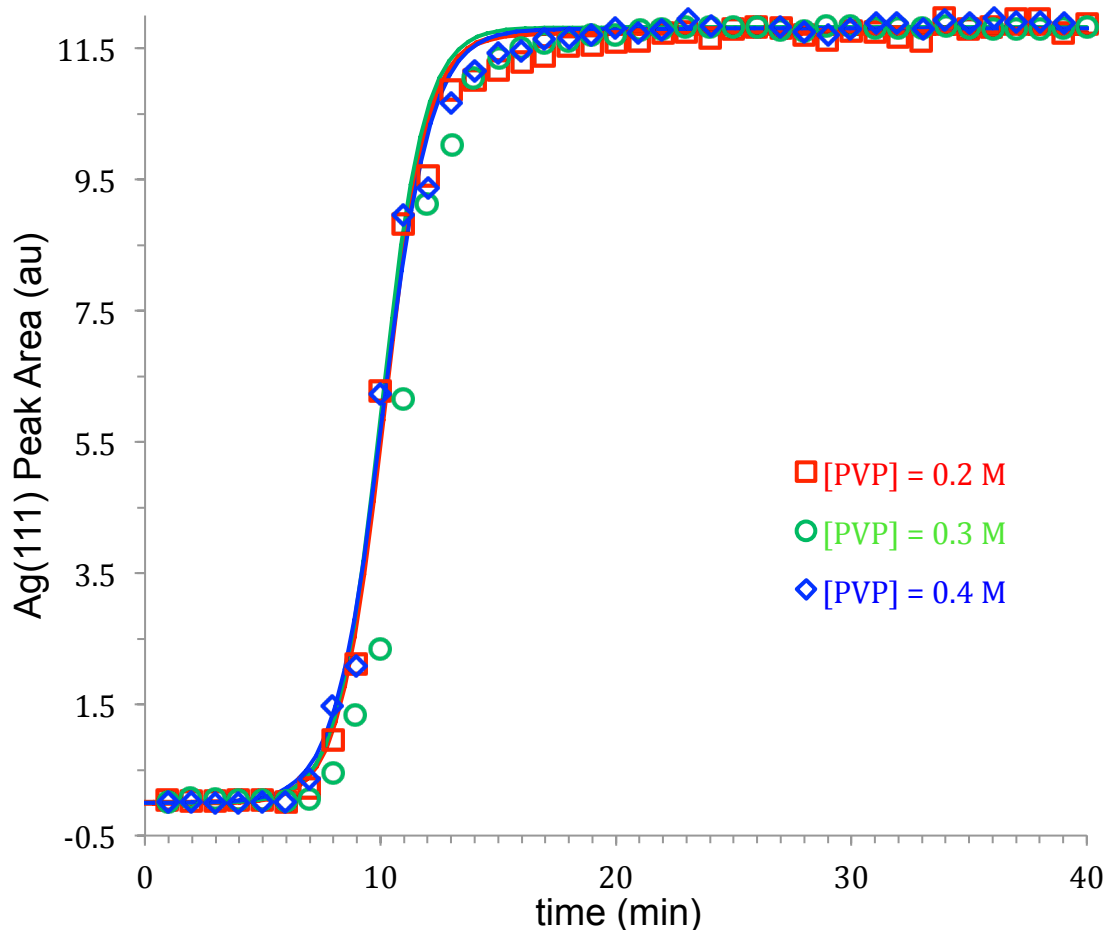
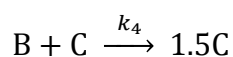
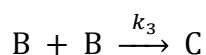


Figure S4. Ag(111) Peak area versus time plot for the formation of Ag(0) nanoparticles from the polyol reduction of silver(I) ions in the presence of PVP stabilizer in various concentrations at 140 °C under microwave heating. The peak area kinetics data in Figure S11 in the Supporting Information of the 2016 paper⁵ were used. The kinetics data are well-fit by the 2-step FW mechanism,⁶ yielding the rate constants k_1 and k'_2 .

S2. Fitting the kinetics data to the Bimolecular Plus Autocatalytic Agglomeration Mechanism

The kinetics data were also fit to the bimolecular agglomeration ($B + B \rightarrow C$; rate constant k_3), and autocatalytic agglomeration ($B + C \rightarrow 1.5 C$; rate constant k_4) steps^{11,12} of a general 4-step mechanism¹³ (eq. S1). This is the proper equation to use *if* one is starting with preformed Ag_n^0 nanoparticles, B (i.e., either starting with preformed nanoparticles deliberately, or perhaps unwittingly as could be the case in the prior work⁵).





$$[\text{C}]_t = \frac{2k_3[\text{B}]_0(1-e^{k_4[\text{B}]_0 t/2})}{4k_3(1-e^{k_4[\text{B}]_0 t/2})-k_4} \quad (\text{S14a})$$

Equation S14a was first derived elsewhere.¹² However, in the present study we have peak area (PA) data, so that equation (S14c) is required, an equation readily derived from equation (S14a) by the replacements $[\text{C}]_t = \frac{\text{PA}_t}{C}$ and $[\text{B}]_0 = \frac{\text{PA}_\infty}{C}$:

$$\frac{\text{PA}_t}{C} = \frac{2k_3 \frac{\text{PA}_\infty}{C} (1-e^{k_4 \text{PA}_\infty t/2C})}{4k_3(1-e^{k_4 \text{PA}_\infty t/2C})-k_4} \quad (\text{S14b})$$

where $k'_4 = k_4 \frac{1}{C}$ (i.e. $k_2 = Ck'_4$, $C = \text{constant}$)

$$\text{PA}_t = \frac{2k_3 \text{PA}_\infty (1-e^{k'_4 \text{PA}_\infty t/2})}{4k_3(1-e^{k'_4 \text{PA}_\infty t/2})-Ck'_4} \quad (\text{S14c})$$

As the plot in Figure S5 shows, the kinetics data are pretty well-fit to equation S14c. This is the expected results, as the discussion in the main text further details. The fit to equation S14c in turn raises the question if the reported kinetics⁵ are actually monitoring the nucleation and growth of Ag^0_n from the starting Ag^+ , (“A”), or if they are really monitoring the agglomeration of Ag^0_n (“B”) preformed relatively rapidly under the reaction conditions.

One final point before leaving Figure S5: the slight overcutting of the data at the end of the induction period in Figure S5 typically can be removed (we know from experience) by fitting to the full, 4-step mechanism (i.e., and with its 2 additional rate constant fitting parameters). Figure S7 (*vide infra*) documents this predicted better fitting of the post-induction period “turn-on” using the 4-step mechanism and the same data as fit in Figure S5.

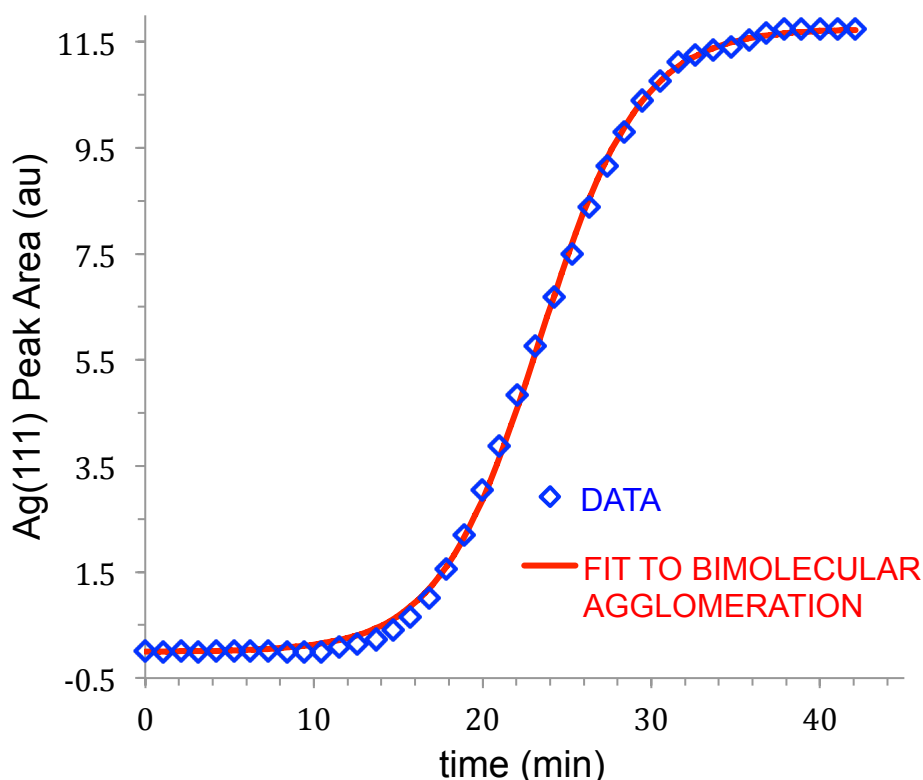


Figure S5. Ag(111) Peak area versus time plot for the formation of Ag(0) nanoparticles from the polyol reduction of silver(I) ions in the presence of PVP stabilizer with microwave heating at 140 °C (obtained from the peak area of Ag(111) reflections in Figure 2A of the 2016 paper⁵). The data are well-fit to the bimolecular agglomeration and autocatalytic agglomeration steps¹² that are the last two steps of the 4-step mechanism detailed elsewhere,¹³ yielding the rate constants $k_3 = (3.5 \pm 0.3) \times 10^{-4} \text{ min}^{-1}$ for the bimolecular agglomeration and $k'_4 = (2.84 \pm 0.05) \times 10^{-2} (\text{au})^{-1} \text{ min}^{-1}$ for the autocatalytic agglomeration with a reduced Chi-Sqr = 1.29×10^{-2} , and $R^2 = 0.99949$. An initial value of $[B]_0 = 2 \times (11.74) / \text{constant M}$ (i.e., $\text{PA}_\infty = 2 \times (11.74) \text{ au}$) is used because of the $3B \rightarrow 1.5 C$ (i.e., equivalently $1B \rightarrow 0.5 C$) stoichiometry for the reaction in eq. S13 above (i.e., and not $B]_0 = (11.74) / \text{constant M}$ as employed elsewhere in this work, where the net stoichiometry is $2A \rightarrow 2B$ (i.e., equivalently $1A \rightarrow 1B$)).

S3. Estimation of the Fraction of Surface Atoms in a 100 nm Ag(0)_n Nanoparticle

The total number of atoms in a 100 nm Ag(0)_n nanoparticle is estimated to be $N(\text{total}) = 3.1 \times 10^7$ atoms using Equation S15.¹⁴

$$N(\text{total}) = \frac{\pi D^3 \rho N_A}{6 MW} \quad (\text{S15})$$

where D is diameter of nanoparticle in cm, ρ is the density of silver = 10.49 g/cm^3 , N_A = Avogadro's Number = 6.022×10^{23} , and MW is the molecular weight of silver = 107.8682 g/mol .

The number of surface atoms can be estimated in a couple different ways; what follows are rough estimate that, however, are more than sufficient for what we need—a semi-quantitative illustration that only a small fraction of the total Ag(0) atoms in a ~100 nm Ag(0)_n nanoparticle are on the nanoparticle's surface. A first estimate of the number of surface atoms can be obtained by dividing the surface area of spherical particle with diameter D by the area occupied by one silver atom (diameter d), buy realizing that touching, close-packed circles have a void area between the circles that can be taken into account by using a square area of d^2 instead of circular area, $\pi(d/2)^2$:

$$N(\text{surface}) = \frac{\text{surface area of spherical particle}}{\text{area occupied by one atom}} = \frac{4\pi(D/2)^2}{d^2} \quad (\text{S16})$$

Using the radius of a silver atom (144 pm),¹⁵ equation S16 gives an estimated number of silver atoms on the surface of silver nanoparticle of diameter 100 nm as $N(\text{surface}) = 3.8 \times 10^5$ atoms.

Dividing the number of surface atoms by the total number of atoms present in the 100 nm Ag(0)_n particle results in a fraction of surface atoms of 0.013 (1.3%).

Alternatively and as a check, the number of surface atoms can be found by considering the number of Ag atoms that would be in the outer-most shell of a large magic number nanoparticle of 100 nm. The solution of Equation S17¹⁶ yields $n = 209$ as the number of shells for a spherical particle with $N(\text{total}) = 3.07 \times 10^7$ atoms.

$$N(\text{total}) = \frac{1}{3}(10n^3 + 15n^2 + 11n + 3) \quad (\text{S17})$$

Using Equation S18,¹⁶ one estimates the number of surface atoms $N(\text{surface}) = 4.4 \times 10^5$ in the 209th shell of the particle.

$$N(\text{surface}) = \frac{1}{3}(30n^2 + 6) \quad (\text{S18})$$

Note that both methods give the same result, ca. 4×10^5 atoms, as an estimate for the number of surface atoms, providing confidence in the estimate, especially for the purposes it is used herein, simply to demonstrate that a very small, ca. 0.013 (1.3%) fraction, of the total Ag(0) atoms are on the surface of such a large, ~100 nm Ag(0)_n nanoparticle.

S4. Issues Related to the Use of the FW 2-Step Mechanism for Analyzing the Kinetics of Formation of Very Large Nanoparticles, and the Rate Constants That Result

We thank Dr. Sun for sharing his thoughts, comments, questions, and concerns on a penultimate version of the main text and SI. We have used his comments and questions, including paraphrasing them and combining them with our own thoughts and reflections in a number of cases, to construct the following discussion. It is our hope that what follows will be useful to future users of the FW 2-step or other, deliberately initially minimal mechanisms as they strive to understand complex dynamic processes in nature. The discussion which follows builds off of Platt's classic 1964 *Science* paper about how to best and most efficiently explore the unknown via a disproof-based scientific method.¹⁷

(1) Question / Issue: *Can the FW 2-step mechanism be used to describe quantitatively the overall formation reaction of large metal nanoparticles, especially if the surface atoms are just a small fraction of the total number of metal(0) atoms. Does it make sense to use the FW 2-step mechanism for larger nanoparticles, especially in a quantitative way?*

Discussion: This valid concern derives from the fact (i.e., the estimation already provided, *vide supra*) that in a relatively large ~ 100 nm Ag_n particle, there is something like $\sim 3 \times 10^7$ Ag atoms, but only $\sim 4 \times 10^5$ of those atoms on the surface. Hence, only 0.013 (1.3%) of the total Ag atoms are present on the surface of the final, ~ 100 nm nanoparticle. Several comments and thoughts seem relevant here:

(i) First, the FW 2-step mechanism has been used to account quantitatively for the formation kinetics of particles of many sizes, including particles at least 1.7-2.0 nm Ir(0),¹⁸ 3-5 nm Rh(0),¹⁹ Pd(0) particles as large as 7.2 nm,²⁰ and Au(0) as large as 18 nm.²¹ The present ~ 100 nm Ag(0) particles⁵ are, then, “only” ~ 5 -times larger than the prior largest nanoparticle treated by the FW 2-step mechanism. While this does not necessarily mean that the FW 2-step mechanism will automatically be applicable, the above-noted precedent in turn does not argue that the 2-step mechanism is automatically inapplicable to larger nanoparticles. One simply needs to try fits to the 2-step mechanism, see what results, and then be careful and thoughtful in interpreting the results.

(ii) Hence, second and importantly, then, is the experimental finding in the main text and the SI of the present contribution demonstrating that the FW 2-step mechanism can quantitatively account for the sigmoidal kinetics curves in the 2016 paper. All of them, and even though $\sim 10^7$ atoms are moved thorough the underlying true elementary step mechanism in what must, then, be $>10^7$ actual elementary steps! This is, no doubt, one of the interesting findings from the present reanalysis. From those experimentally observed good fits it follows that (a) either the FW 2-step mechanism is able to describe the kinetics of formation of such large, ~ 100 nm Ag_n particles in at

least an average way, *or* conceivably (b) that the HEXRD monitoring is not actually following the nucleation and growth of a ~ 100 nm particle, but, rather, is following something different, such as agglomeration of already formed Ag_n , “B” nanoparticles, a possibility discussed in the main text and supported in a general way by the fits shown above in Figure S5 to the $\text{B} + \text{B} \rightarrow \text{C}$, then $\text{B} + \text{C} \rightarrow 1.5 \text{C}$, 2-step agglomeration mechanism. If, then, the actual reaction is primarily *agglomeration*, then any worry stated about the applicability of the FW 2-step mechanism to the *nucleation and growth* of the present, ~ 100 nm Ag_n particles becomes moot.

(iii) A third and rather important point is if you don’t use the FW 2-step mechanism (or 2-step agglomeration mechanism, or try the 3- or 4-step mechanisms, *vide infra*), one quickly runs up against the issue of what mechanism and associated well-defined differential equation(s), then, can one use to analyze the sigmoidal kinetics data? The present work shows that using an empirical function is not the answer, as discussed a bit more in the next point (iv) below.

(iv) Fourth, we now know that using an empirical sigmoidal function failed to yield even *qualitative* results that made physical sense, much less reliable *quantitative* results. The fact of the matter is that the FW 2-step (and 3- and 4-step, *vide infra*) mechanisms are presently—sadly, if you like!—state-of-the-art for *at least first-pass fitting and analysis* of sigmoidal growth curves across nature. This statement is presently true even if the particles are ~ 100 nm and even if one then has considerable worry about, for example, what the resultant, highly averaged, especially k_2 rate constant means (a bit more on that valid concern in a moment).

(v) Fifth, even if one believes that the FW 2-step mechanism is somehow ill-suited for a sigmoidal growth curve at hand, a very important point here is that one’s responsibility as a scientist is still *to experimentally test* that belief; to try to show that the 2-step (or 3- or 4-step) mechanisms do not work, or that they are somehow inapplicable. One cannot just dismiss outright the 2-step mechanism—that is, just dismiss any reasonable, precedented mechanism outright—as to do so falls under the category of Confirmation Bias.²² Confirmation bias (also called “myself bias”) is that well-chronicled, improper way of thinking in which one basically has intellectual blinders on and gathers only the data that is consistent with one’s original idea (i.e., one’s initial bias; one’s original hypothesis). As a scientist, our job is to try to disprove all reasonable alternative hypotheses, *especially and starting with our own pet, initial hypothesis*, as taught in Platt’s classic paper on a proper scientific method.¹⁷ In the present example, if one’s initial hypothesis is that the FW 2-step mechanism cannot be applied to large nanoparticles, then the first step experimentally for proper, reliable, disproof-based science is *to try* the 2-step mechanism, and see whether or not it can account for the data. One must test one’s *belief—one’s religion*—that it cannot. The fact is that

the FW 2-step mechanism can account for all the HEXRD kinetics data, and quantitatively so, even if issues exist with how to interpret, or how useful, the resultant especially k_2 values are.

(vi) However, precisely what the good fits to the FW 2-step mechanism demonstrated in the present contribution mean is still an open. It may well be that the good fits to the FW 2-step mechanism are indicating that the HEXRD monitoring⁵ is not following much if any of nucleation and growth, but, rather, is monitoring mostly agglomeration of preformed, “B” type nanoparticles. Restated, what the “starting material” actually is for the purposed of the HEXRD monitoring performed is not clear at present. This issue ties in to the answer to the question in a section that follows, namely the importance of catching scientific phenomena *first* in a logical, conceptual box¹⁷ (e.g., a proper mechanistic or other model), and only then worrying too much about quantitation of the parameters of that model.

(vii) Next, it merits mention that our original 1997 paper⁶ provides a “scaling factor” as an average way to treat the number of surface atoms out of the total number of atoms in a growing nanoparticle. Importantly, a continuous function that can accomplish the same correction, only continuously and hence better, has been reported by others.²³ Hence this “scaling issue”, recognized in our very first, 1997 FW 2-step mechanism paper,⁶ can be dealt with at least in principle by the published methods.^{6,23} That said, as the number of surface atoms becomes a smaller and smaller percentage of the total atoms (as in a 100 nm nanoparticle), the surface growth step becomes less and less autocatalytic, going from an initial $A + B \rightarrow 2 B$ form to a limiting $A + B_n \rightarrow B_{n+1}$ form, where n and $n+1$ become insignificantly different in the case of n values much greater than 1 (see footnote 6 elsewhere⁴¹ that bears on this discussion). In that sense, it would appear to be true that the FW 2-step mechanism is fundamentally more applicable to smaller than to larger nanoparticles, *or at least to the initial phase of the formation of larger particles*. We thank Dr. Sun for sharing his thoughts and discussion on this point, insights that made us think more deeply and carefully about the pros and cons of applying the FW 2-step mechanisms to large, ~100 nm nanoparticle formation reactions.

What is quite interesting here, on reflection, is why, then, does the 2-step mechanism fit the observed HEXRD data so well for the formation of such a large, ~100 nm $Ag(0)_n$ particle? What is this really telling us? In words and phenomenologically, the $A \rightarrow B$ then form $A + B \rightarrow 2 B$ form (or the $B + B \rightarrow C$ then $B + C \rightarrow 1.5 C$ form if agglomeration is most what is being monitored) is able to capture the primary kinetic aspects of the HEXRD-based monitoring of even very large, ~100 nm $Ag(0)_n$ particles, even including the averaging from $n = 1$ to $n = 10^7$ (!) that is, apparently, accomplished primarily within the k_2 rate “constant”.

(viii) Finally to end this first section, we offer the perspective that the questions and concerns above are really just the usual *research opportunities*! It is of considerable interest to compare experimentally—with suitable reflection and caution—the rate constants k_1 and k_2 to those for the formation of much smaller, 10-20 nm Ag(0)_n nanoparticles. A starting hypothesis (educated guess^{18,24,25}) here is that the k_1 will be less variable than k_2 . Indeed, our recent literature^{18,24,25} suggests that low-molecularity nucleation may be relative constant across nucleation in nature and, if so, then possibly relative constant across very different nanoparticle sizes. If so, then the k_1 value will be more reliable compared to the k_2 value than may be the most variable on going from smaller to larger nanoparticles (with care to form them under conditions as identical as possible while still allowing different particle sizes to be formed). A related question meriting testing is *how well or poorly does the scaling factor correction of k_2 work?* What, really then, are the issues in using the only good, presently available, minimalistic, disproof-based (2-step) mechanism on very large, ~100 nm particles and in comparison to much smaller, many-fewer-atom-containing, 10-20 nm particles? Why does the 2-step mechanism do such a good job of fitting the kinetics data for the formation of such large nanoparticles?

(2) Question / Issue. *Is the fitting sensitive to k_1 , and what about the large errors that in general one tends to see for k_1 values from the 2-step mechanism?*

Discussion: The first point to make here is that, based on the use of the 2-step mechanism herein and the discussion provided just above, an even better question here is probably what is the uncertainty in k_2 ?

But, addressing the question posed of the general uncertainty in determining k_1 values, the first piece of evidence on this question is Figure S6 below which show that the overall sigmoidal curves are at least reasonably sensitive to the value of k_1 . Hence, one really needs to be specific and quantitative about what level of uncertainty one is worried about? Also, is that stated level of uncertainty more or less than the minimal uncertainty ever measured for any nucleation event for any system in nature? (A bit more on this later point in a moment.) One other point to make here and upfront is that larger amounts of more precise data go a long way to reducing the uncertainty in all rate constants, and certainly in k_1 and k_2 from fitting sigmoidal curves are no exception.

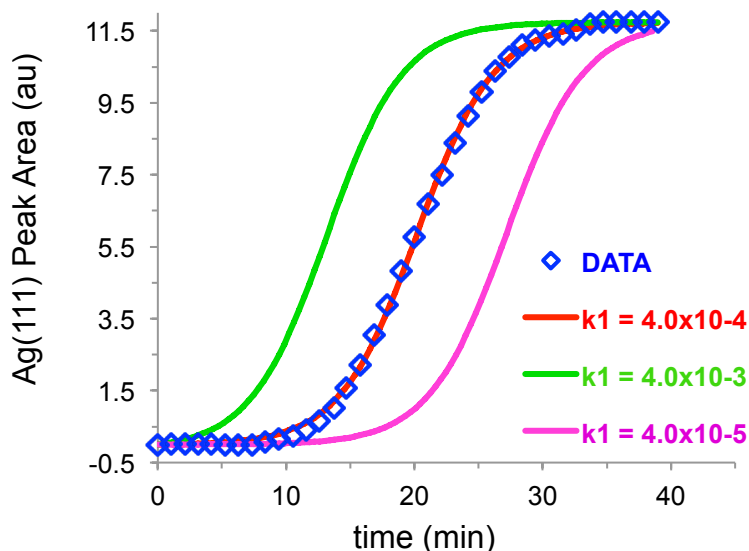


Figure S6. (Blue diamonds) Ag(111) Peak area versus time data obtained from Figure 2c in the main text. (Red solid line) Fit of the data to the FW 2-step mechanism⁶ yielding $k_1 = (4.0 \pm 0.3) \times 10^{-4} \text{ min}^{-1}$ and $k'_2 = (2.83 \pm 0.04) \times 10^{-2} (\text{au})^{-1} \text{ min}^{-1}$. (Green solid line) The simulation by using the FW 2-step mechanism with $k_1 = (4.0 \pm 0.3) \times 10^{-3} \text{ min}^{-1}$ and $k'_2 = (2.83 \pm 0.04) \times 10^{-2} (\text{au})^{-1} \text{ min}^{-1}$ as input. (Pink solid line) The simulation by using the FW 2-step mechanism with $k_1 = (4.0 \pm 0.3) \times 10^{-5} \text{ min}^{-1}$ and $k'_2 = (2.83 \pm 0.04) \times 10^{-2} (\text{au})^{-1} \text{ min}^{-1}$ as input. Note the sizable change in the resultant curve when the k_1 rate constant is varied by a factor of 10 while keeping the value of k'_2 constant. In short, the results in this figure reveal that the observed kinetics curve is at least reasonably sensitive to the value of the nucleation rate constant, k_1 .

However, to further and more broadly address the question raised above (i.e., about uncertainty in any variable one might be measuring), in science, one in general needs to capture and understand the conceptual and qualitative parts of the problem *first*, before worrying too much about obtaining the highest precision quantitation of the parameters of that phenomenon. Platt, a physicist, talks about this in his classic 1964 paper on a preferred scientific method;¹⁷ he notes the need to catch phenomena first in a “logical box”, and *only after that* in a “mathematical box”. Insightfully, he goes on to say: “The logical box is coarse but strong. The mathematical box is fine-grained but flimsy. The mathematical box is a beautiful way of wrapping up a problem, but it will not hold the phenomenon unless they have been caught in a logical box to begin with”. Important to realize here is that Platt was talking to a physics convention at the time about why he felt biologists were making faster strides in their endeavors than were physicists in their research areas.

Consistent with Platt’s directive, experience as well as reflection on the biggest findings in science reveal that those paradigm shifts in the T. Kuhn sense are often qualitative (although many times very precise, quantitative data are needed to support those qualitative concepts and to rule out

alternative hypotheses). Consider gravity; evolution; whether or not the earth is round vs flat; whether “Cold Fusion” exists, and so on. Such general concepts are the broad, most important, ones transforming human thinking and beliefs.

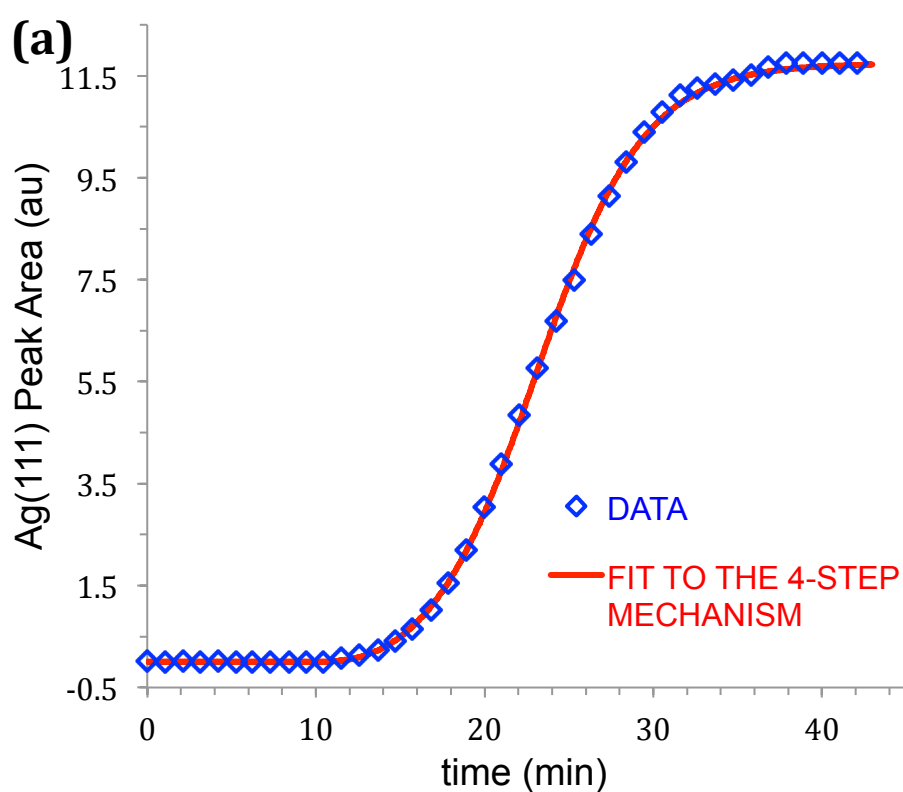
Fully consistent with this, *the most important aspects of the FW 2-step mechanism are its two key conceptual components that were both novel at the time of its 1997 publication⁶: slow, continuous nucleation, and fast autocatalytic surface growth.* These two concepts, in the form of balanced chemical equations that define these concepts, the words that can be used to discuss the concepts, and the corresponding rate constants are the two key conceptual, mechanistic components (or “logical boxes” as Platt calls them) of the FW 2-step mechanism. Those balanced reactions and thereby rigorously defined associated differential and integrated rate equations, and the rate constants, k_1 and k_2 , are what allows one to deconvolute sigmoidal curves into the two components of typically slow, continuous nucleation, and fast autocatalytic surface growth, regardless of the precision for the resultant two rate constants in a given system.

Telling in the present example is how Platt’s point—about one having to nail down the conceptual, “logical box” first—is right on the mark for both the present and the prior study⁵: even with the present reanalysis, no one is 100% sure of what is actually being measured by HEXRD (i.e., other than it is measuring the formation of crystalline, diffracting $\text{Ag}(0)_n$). Is it actually nucleation and autocatalytic growth that is being monitored as cited in the 2016 study? Or, is the HEXRD (that needs larger, crystalline particles before they can be detected—witness the left-most part of Figure S2) mostly monitoring bimolecular nucleation of agglomeration, and autocatalytic agglomeration of nanoparticles quickly preformed under the reaction conditions, as one alternative hypothesis and associated set of concepts here? This latter hypothesis, that it is mainly agglomeration that is actually being monitored, is consistent with the good fit to the 2-step agglomeration mechanism in Figure S5. But, disproving or supporting it requires knowing if one is starting with A (Ag^+) or B (quickly formed Ag^0_n) for the purposes of the HEXRD monitoring. Or, is the 4-step mechanism really a better description of the main physical processes present, a second alternative hypothesis meriting deeper examination. The improved fit in Figure S7 over that in Figure S5 is at least some initial evidence in support of this second alternative, mechanistic hypothesis. In short, it is by no means obvious what precise chemical processes are being monitored by HEXRD other than to say that it is the formation of crystalline $\text{Ag}(0)_n$ the ends up at ~ 0.1 micron sized particles.

Platt is, then, completely correct and even though his 1964 paper precedes the present case study by 53 years: still unclear are even the exactly correct (qualitative!) concepts and associated

“logical box” to best account for the main chemical reactions responsible for and consistent with the elegantly obtained HEXRD kinetics data.

One thing, then, is for sure here: it is a bit too soon to be worrying too much about the uncertainty in k_1 . We first need to know what reaction we are monitoring. Additionally, it is certainly premature, as well as inappropriate science, to dismiss *any* mechanism from testing because of any preconceived worry about the precision of the resultant rate constants. In a “cart before or after the horse” analogy, the horse here is the (qualitative) logical box (the precise reaction and its minimal mechanism), and that has to pull and come before the cart (the quantitative, high-precision rate constants).



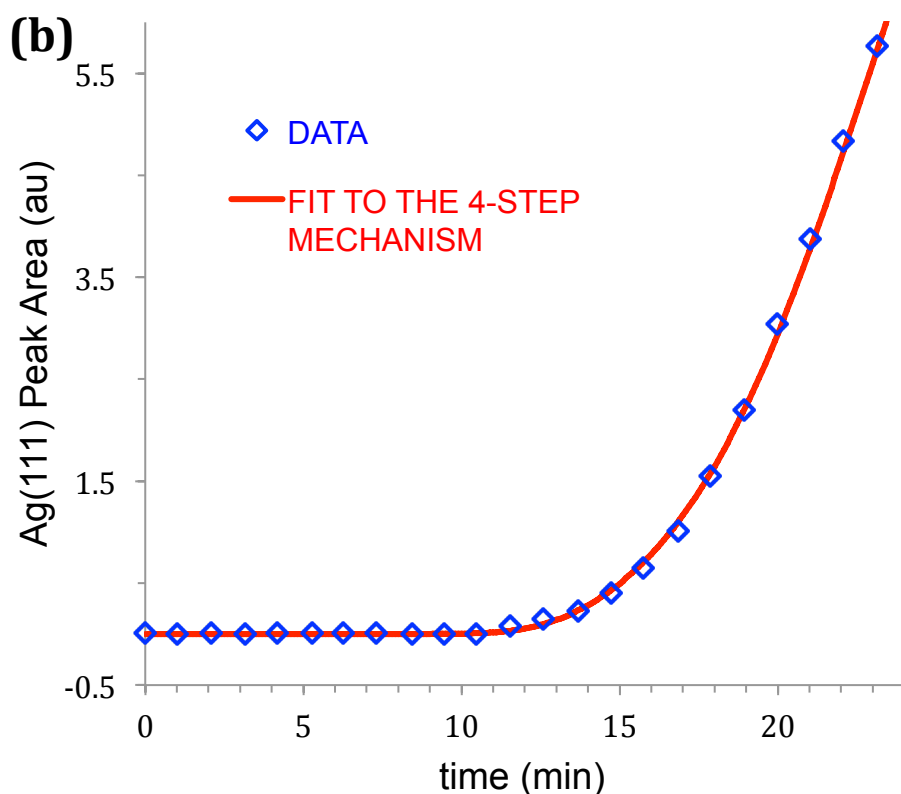


Figure S7. (a) Ag(111) Peak area versus time plot for the formation of Ag(0) nanoparticles from the polyol reduction of silver(I) ions in the presence of PVP stabilizer with microwave heating at 140 °C (obtained from the peak area of Ag(111) reflections in Figure 2A of the 2016 paper⁵). The data are well-fit to the 4-step, double-autocatalytic mechanism for transition-metal nanoparticle formation consisting of: slow continuous nucleation, $A \rightarrow B$ (rate constant k_1), fast autocatalytic surface growth, $A + B \rightarrow 2B$ (rate constant k_2), bimolecular agglomeration, $B + B \rightarrow 2B$ (rate constant k_3), and then autocatalytic agglomeration step between smaller particles (B) and what appear to be larger, more bulk-metal-like (C) particles, $B + C \rightarrow 1.5C$ (rate constant k_4) as detailed elsewhere,¹³ yielding the rate constants $k_1 = 3.3 \times 10^{-5} \text{ min}^{-1}$, $k_2' = 3.8 \times 10^{-2} (\text{au})^{-1} \text{ min}^{-1}$, $k_3 = 2.3 \times 10^{-4} \text{ min}^{-1}$, and $k_4' = 2.7 \times 10^{-2} (\text{au})^{-1} \text{ min}^{-1}$. An initial value of $[A]_0 = 2 \times (11.74) / \text{constant M}$ (i.e., $PA_\infty = 2 \times (11.74) \text{ au}$) was used in the fit as described in the caption of Figure S5. **(b)** The same plot as in (a) but with the induction period expanded to illustrate the considerably better fit in this area (and compared to examining Figure S5 in the same, post induction period area).

The above said, before leaving the topic of measuring precise rate constants, the reader interested in learning more about why it is notoriously hard to measure precise nucleation rate constants is referred to our recent publications.^{1,18,24} Those publications cite literature with the highest precision rate constants measured for nucleation anywhere across nature. Those publications also detail the error in our own k_1 and k_2 measurements analyzed over a multi-year period and over the course of multiple investigators (ca. $\pm 10^{1.2}$ and $\pm 50\%$ for k_1 and k_2 , respectively) including the known chemical and other reasons for those experimentally based error

bars—which are actually some of the most precise rate constants measured for nanoparticle nucleation and autocatalytic growth. Those publications detail additional, related issues, including the involvement of simple room dust that, alone, can make the k_1 nucleation rate constant faster by a factor of ~ 5 to 7.6 , dust which if removed by microfiltration narrows the resulting size distribution of the nanoparticles by a remarkable ~ 2.4 fold!²⁴

Hence, yes, measuring more precise rate constants for conceptually well-supported, disproof-based mechanisms is an important topic meriting future effort. But, precise rate constants are not yet a top priority in the nucleation, growth, and agglomeration field, a field where there is still much qualitatively and conceptually that we don't yet know, especially about nucleation.

Finally, to demonstrate that precise rate parameter measurements are a more general problem, one not constrained to the FW 2-step mechanism as the question posed at the start of this section tends to imply, one can raise the related question of “what are the almost surely larger uncertainty / errors in the 4 total (apparently) fitting parameters of the empirical equation used in the 2016 paper?”. We say almost surely larger errors (compared to the relative error in k_1 from a FW 2-step fit) because the empirical function used has 2 additional parameters (4 total, or so it would appear⁵) in comparison to just 2 rate constant parameters, k_1 and k_2 , in the FW 2-step mechanism, and for the same number of data points being examined in each fit. *Precise parameters from fitting sigmoidal curves are an issue in our experience no matter what functions are being used.* Relevant to this point is that we have recently published mathematical derivations showing that all parts of a sigmoidal curve well-fit by the FW 2-step mechanism are a function of *three* parameters, k_1 , k_2 , and the precursor's starting concentration, A_0 .¹

(3) Question / Issue: An issue that has come up is that local superheating phenomenon is believed to occur in at least some microwave reactions, so that very high temperatures, much higher than the measured solution temperature, can putatively exist, at least in microenvironments and for short periods of time. Hence, does this invalidate the application of the FW 2-step mechanism that was developed for, and to date has been primarily applied to, solution reactions heated in the normal way?

Discussion: While microwave heating is, we agree, a complication for determining mechanism (mechanistic determination that is best done isothermally, changing temperature one experiment at a time), this potential issue in no way invalidates the logic of seeing if the 2-step mechanism can fit the nanoparticle formation kinetics data obtained by microwave heating (i.e., seeing if the prior best studied and most widely applied mechanism of formation for nanoparticles

can fit the observed data). Of course we now know that the 2-step mechanism actually *can* fit all the data in the 2016 paper, without the need to resort to an empirical sigmoidal fitting function.

The mechanism of microwave heating is another question. One can imagine experiments where the microwave power and rate of addition is varied, and using fits to the 2-step mechanism to try to tease out an answer to the above questions. That said, our own approach to the question of potential complexities added by the microwave heating method would be to (i) first have a careful look at the extant microwave heating literature, with then (ii) an eye towards studies of and a focus on much simpler systems than a $>10^7$ elementary step nanoparticle formation reaction.

Note Added in Proof: see reference 58 that has just appeared, which studies Ni and Au nanoparticle (NP) formation under microwave (MW) heating, and concludes: “The power-dependent enhancement in the dispersity for NPs grown in a MW (microwave) is readily explained within the FW autocatalytic mechanism without involving MW special effects”.⁵⁸

(4) Question / Issue. *An important part of the 2016 paper is the direct support for nanoparticles coalescence provided therein, where the size variation grew faster than expected for the cube root of the Ag mass (i.e., expected if no coalescence / agglomeration is present). Specifically, the nanoparticle size at 35 minutes is larger than expected when calculated from the size at the short time of 15 min. (We acknowledge and thank Dr. Sun once again for these specific insights.) Hence, coalescence / agglomeration appears to be present.*

Discussion: This is why we used the best available, most disproof-based, 4-step mechanism^{13,28,29} (that contains 2 types of agglomeration / “coalescence”) to try to fit the data, as successfully reported in Figure S7 which follows. This is also why we tried to, and were successful in, fitting the data (albeit not quite as well) with just the 2 agglomeration steps from that 4-step mechanism, that is with just $B + B \rightarrow C$, then $B + C \rightarrow 1.5 C$, as we successfully done in Figure S5.

Restated, yes, “the elephant in the room” in both the 2016 paper and the work reported in the present contribution is, as discussed also in the main text, if the reaction being followed is “nucleation and growth of Ag_n^0 ”, or is that assertion fundamentally incorrect / misformulated? Is what is really occurring, instead, primarily the reactions and associated concepts of nucleation of *agglomeration*, then autocatalytic *agglomeration* of rapidly preformed $Ag_n^0 (= B)$, $B + B \rightarrow C$, then $B + C \rightarrow 1.5 C$, as a fit to just these 2 steps back in Figure S5 demonstrates is consistent with the data—depending on if one is really starting with “B” (Ag_n^0), or “A” (Ag^+), for the purposes of the HEXRD monitoring is actually detecting. The fact that HEXRD requires crystalline material of a size of ~ 9.9 nm for a decent signal to be generated *means that we are way beyond the nucleation*

and growth of the smallest nanoparticles—at about $\sim 3 \times 10^4$ Ag(0) atoms and more as the stage of what we have recently termed the First Observable Cluster (FOC)²⁵ by whatever monitoring method is being employed.²⁵ Indeed, when the reaction is over, ~ 100 nm particles have formed that contain around 10^7 Ag(0) atoms. The improved fit to the 4-step mechanism in Figure S7, and which includes two types of agglomeration, is the first firm kinetics evidence that agglomeration (“coalescence”) is at least part of the correct story. Hence, the present analysis and the 2016 paper are in close accord on the existence of agglomeration being part of the formation of the ~ 100 nm Ag(0)_n particles.

Actually, reflection makes apparent that it is almost unthinkable that a ~ 100 nm particle can be formed without any agglomeration. The literature is consistent with this point, a paper from Professor W. Buhro’s group noting “the prominent role of aggregative growth”²⁶ for the specific case of Ag(0)_n nanoparticles formed from “a molecular precursor”,²⁶ a system conceptually closely analogous to the also Ag(0)_n particles formed in the 2016 study. Additional experiments are needed and would be welcome determining what is actually being monitored by the otherwise powerful, *in situ* HEXRD method.

(5) Question / Issue. *Even if the time-dependent profile can be well fit with the FW 2-step mechanism, is this really only a mathematical fitting exercise? Isn’t it the more detailed, more complex, fundamental (elementary) steps that one is after, such as but not limited to, ion reduction, metal-atom adsorption, metal-atom diffusion, catalysis by surface or other metal atoms, non-uniform active sites, nanoparticle coalescence, and so on?*

Discussion. “Only a mathematical fitting” is the troubling phrase in the above question as we have posed it. We have “only” attained a firm, disproof-based, non-empirical, mechanistic start on a reaction that has $>10^7$ individual steps in the present 100 nm Ag(0)_n nanoparticle formation reaction.

The above question, however, is pedagogically useful in that it misses completely the main point and the main conceptual strength of the FW 2-, 3-, and 4-step mechanisms: because of the high level of disproof that has gone in to attaining the FW 2-,⁶ 3-²⁷ and 4-step^{28,29,30,31} (over alternative models disproved in the 4-step mechanism, for example,²⁸ a model that contains as its first 2 steps the 2-step model), and the fact that the 2-, 3-, and 4-step mechanisms were developed to obey Ockham’s razor, they are *not* just a fitting exercise. Rather, the evidence supports the idea that they are considerably more fundamental and more basic than that—they are the “logical” and “conceptual boxes” of the type Platt says must come first and foremost in science.¹⁷ Their rigorous,

disproof-based and Ockham's razor development over a ≥ 25 year period is a main reason why these deliberately minimalistic mechanisms are enjoying wide use by others to fit a broad range of sigmoidal growth and aggregation curves across nature. Their current usage stands at over 800 citations presently for the combined 2-, 3-, and 4-step mechanisms, for a range of diverse systems, including, but not limited to, "only" the following systems as lead references: in homogeneous catalyst formation,^{32,33,34} heterogeneous catalyst formation,^{35,36,37} protein aggregation,^{38,39,40,41} solid-state kinetics,^{42,43} dye aggregation,⁴⁴ and other areas of nature showing "cooperative", autocatalytic phenomena such as, intriguingly, impurity uptake by resins used for water purification.⁴⁵ The examples in just nanoparticle formation reactions include: Ir(0),^{6,28,46} Rh(0),^{47,48,49,50} Pt(0),^{28,51} Ru(0),⁵² Pd(0), Ni(0),⁵³ Ag(0),⁵⁴ and Au(0),^{55,56} nanoparticles, including direct XAFS support for the 2-step mechanism in the cases of⁵⁰ Rh(0) and⁵¹ Pt(0) nanoparticles, and direct SAXS support for the 2-step mechanism in the case of Ni(0) nanoparticles.⁵⁰ Noteworthy from the above list is the prior use of the FW 2-step mechanism for Ag(0) nanoparticles,⁵⁴ precedent directly relevant to the 2016 study.

Unfortunately and to be completely truthful, the main example we have of something that is "*only a mathematical fitting exercise...*" is what was done in the 2016 paper, namely using a mechanistically not just worthless, but misleading, empirical fitting function to try to analyze the HEXRD kinetics data—literally nothing more than a "mathematical fitting exercise". Trying to disprove the applicability of the most widely used 2-step mechanism, that already had prior precedent for its applicability to Ag(0) nanoparticles,⁵⁴ would have been a better way to proceed. It is, then and in the end analysis, the amount of disproof that has gone into the FW 2-, 3-, and 4-step mechanisms that make those mechanisms much more than "only a fitting exercise".

The available evidence presently argues strongly that one *must* work to start from a disproof based, simplest possible mechanism that will fit all the data if one has any hope of doing rigorous, disproof-based, and hence reliable chemical mechanistic studies. This is the history of physical-organic chemistry; this is the history of mechanistic science in general. That disproof of all reasonable alternative mechanisms—that is, disproof of all reasonable alternative hypotheses—is also the essence of the scientific method and its associated epistemology. That history of science demands that one disprove.¹⁷ The failure to do so is far too prevalent in many papers that one reads in "modern" "science", in our opinion.

The requirement that one examine and try to disprove all reasonable alternative hypotheses, combined with the fact that disproof is often tedious and sometimes not possible with current methods and techniques, means that one is in turn often left with more than one remaining hypothesis (e.g., more than one non-disproved mechanism) that one must somehow deal with. One

must then turn to the conditional exclusion permitted by the philosophical position known as Ockham's razor to pick, conditionally at the time, the simplest model / mechanism—but, again, only conditionally and until new, more powerful methods to test those excluded hypotheses are developed and until new, additional evidence becomes available that *demand*s a more complex mechanism. A good place to start to read further discussion of these points, with references to R. Hoffmann and co-workers excellent expositions on Ockham's razor and its conditional exclusions (only), is the SI available elsewhere.⁵⁷

Lastly but not least, the hypothesis of “only represents a mathematical fitting” exercise is soundly disproved by the following, single example. That example is one in which a fit to the 2-step model allowed discovery of the otherwise hidden catalyst (“B”), then also the discovery of the full catalytic cycle including the underlying elementary-steps of that catalytic cycle. The system is one world-expert mechanistic scientists were otherwise stuck and out of ideas of how to achieve knowledge of the underlying catalyst and elementary step catalytic cycle.³⁴ Importantly, the discovered elementary steps add up to the general form of the 2-step mechanism ($A \rightarrow B$, then $A + B \rightarrow 2B$), revealing why the use of a fit to the 2-step pseudo-elementary step mechanism was able to—indeed in this case the required first step for—discovering the underlying, true elementary step mechanism. In addition to that telling example,³⁴ several other recent examples^{43,55,56} exist where initial fits to the 2-step mechanism proved necessary en route to subsequently discovering underlying chemical steps. In one case, the author of that paper noted the insights they were able to attain went far beyond those possible by a fit to the *empirical* Avrami equation.⁴³

The evidence, then, not only disproves the hypothesis of “...only represents a mathematical fitting exercise”, the evidence in the relevant literature actually supports the *opposite* hypothesis if one take the time to gather, read, and reflect upon that highly relevant literature. Indeed, fits to the 2-, 3- or 4-step mechanisms (i.e., and where they give the best accounting of sigmoidal kinetics data compared to other models that can be tried) appear by all the available evidence *to be the required first step* en route to the desired, disproof-based, closer to elementary step mechanism(s) of systems displaying sigmoidal kinetics curves.

A valuable outcome of the discussion in this part of the SI is that it helps focus the needed additional, future studies of the interesting microwave-driven, Ag^0_n nanoparticle formation system pioneered by the 2016 study and its authors. (i) Is one starting with “A” or with “B”? This is the most important, unanswered question at present about the microwave-assisted formation of $Ag(0)_n$ nanoparticles. (ii) What “conceptual / logical box(es)” best capture(s) the formation of ~100 nm $Ag(0)_n$ nanoparticles is a second, at presently only partially answered question. Is it really

nucleation and growth, or bimolecular and autocatalytic agglomeration, or is the 4-step mechanism that has all of these steps what is really going on kinetically and mechanistically? (iii) A third question, one that is always present (*vide supra*), is what is the more intimate, closer to elementary step mechanism underlying kinetics curves that are well-fit by the 2-, 3-, or 4-step mechanisms? (iv) Fourth, what can be learned from a comparison of the k_1 and k_2 apparent rate constants from fits to the 2-step mechanism (or fits to the 4-step mechanism) as a function of nanoparticle size? Indeed, why do fits to the simple 2-step mechanism work in the first place for particles that contain 10^7 atoms? (v) Fifth, is there anything else that is needed to fully account for larger, ≥ 100 nm particles, especially their size-distributions, as one educated guess here? (vi) Sixth, is the microwave heating method special in any way? Does it introduce any unusual mechanistic features? (See the very recent publication from G. F. Strouse's group for insights into these questions.⁵⁸) Clearly, only a fraction of the needed research has been done on the interesting system first reported in 2016.⁵

References

- ¹ Bentea, L.; Watzky, M. A.; Finke, R. G. Sigmoidal Nucleation and Growth Curves Across Nature Fit by the Finke–Watzky Model of Slow Continuous Nucleation and Autocatalytic Growth: Explicit Formulas for the Lag and Growth Times Plus Other Key Insights. *J. Phys. Chem. C* **2017**, 121, 5302–5312.
- ² Wertz, D. L. Mass Absorption Corrected X-Ray Powder Diffractograms. Part 1: Measuring Pyrite in Powdered Coals. *Powder Diffraction* **1990**, 5, 44–47.
- ³ El Osta, R.; Feyand, M.; Stock, N.; Millange, F.; Walton, R. I. Crystallisation Kinetics of Metal Organic Frameworks From in situ Time-Resolved X-ray Diffraction. *Powder Diffraction* **2013**, 28, S256–S275.
- ⁴ Roselle, P. Quantitative Mineralogical Analysis of Carbonate Sediments by X-ray Diffraction: a New, Automatic Method for Sediments with Low Carbonate Content. *Sedimentology* **1982**, 29, 595–600.
- ⁵ Liu, Q.; Gao, M. R.; Liu, Y.; Okasinski, J. S.; Ren, Y.; Sun, Y. Quantifying the Nucleation and Growth Kinetics of Microwave Nanochemistry Enabled by in Situ High-Energy X-ray Scattering. *Nano Lett.* **2016**, 16, 715–720.
- ⁶ Watzky, M. A.; Finke, R. G. Transition Metal Nanocluster Formation Kinetic and Mechanistic Studies. A New Mechanism When Hydrogen Is the Reductant: Slow, Continuous Nucleation and Fast Autocatalytic Surface Growth. *J. Am. Chem. Soc.* **1997**, 119, 10382–10400.
- ⁷ Espenson, J. H. Chemical Kinetics and Reaction Mechanisms, 2nd Ed., McGraw-Hill, 1995. See p. 58–59 on Parallel and Concurrent Reactions.
- ⁸ Capellos, C.; Bielski, B. H. J. Kinetic Systems, Wiley-Interscience, 1972. See p. 68–71.
- ⁹ Starkey-Ott, L.; Finke, R. G. Transition-Metal Nanocluster Stabilization for Catalysis: A Critical Review of Ranking Methods and Putative Stabilizers. *Coord. Chem. Rev.*, **2007**, 251, 1075–1100.
- ¹⁰ Methfessel, M.; Hennig, D.; Scheffler, M. Calculated Surface Energies of the 4d Transition Metals: A Study of Bond-Cutting Models. *Appl. Phys. A*, **1992**, 55, 442–448.

- ¹¹ Ott, L. S.; Finke, R. G. Transition-Metal Nanocluster Stabilization versus Agglomeration Fundamental Studies: Measurement of the Two Types of Rate Constants for Agglomeration Plus Their Activation Parameters under Catalytic Conditions. *Chem. Mater.* **2008**, *20*, 2592-2601.
- ¹² Finney, E. E.; Shields, S. P.; Buhro, W. E.; Finke, R. G. Gold Nanocluster Agglomeration Kinetic Studies: Evidence for Parallel Bimolecular Plus Autocatalytic Agglomeration Pathways as a Mechanism-Based Alternative to an Avrami-Based Analysis. *Chem. Mater.* **2012**, *24*, 1718-1725.
- ¹³ Finney, E. E.; Finke, R. G. The Four-Step, Double-Autocatalytic Mechanism for Transition-Metal Nanocluster Nucleation, Growth, and Then Agglomeration: Metal, Ligand, Concentration, Temperature, and Solvent Dependency Studies. *Chem. Mater.* **2008**, *20*, 1956-1970.
- ¹⁴ Lin, Y.; Finke, R. G. Novel Polyoxoanion- and Bu_4N^+ -Stabilized, Isolable, and Redissolvable, 20-30 Å $\text{Ir}_{300-900}$ Nanoclusters: The Kinetically Controlled Synthesis, Characterization, and Mechanism of Formation of Organic Solvent-Soluble, Reproducible Size, and Reproducible Catalytic Activity Metal Nanoclusters. *J. Am. Chem. Soc.* **1994**, *116*, 8335-8353.
- ¹⁵ In CRC Handbook of Chemistry and Physics, 77th ed.; Lide, D. R., Frederikse, H. P. R., Eds.; CRC Press: Boca Raton, FL, 1996.
- ¹⁶ Schmidt, A. F.; Smirnov, V. V. Concept of “magic” number clusters as a new approach to the interpretation of unusual kinetics of the Heck reaction with aryl bromides, *Top. Catal.* **2005**, *32*, 71-75.
- ¹⁷ Platt, J. R. Strong Inference. *Science*, **1964**, *146*, 347-353.
- ¹⁸ Özkar, S.; Finke, R. G. Nanoparticle Nucleation is Termolecular and Involves Hydrogen: Evidence for a Kinetically Effective Nucleus of Three, $\{\text{Ir}_3\text{H}_{2x}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\}^{6-}$, in $\text{Ir}(0)_n$ Nanoparticle Formation From $[(1,5\text{-COD})\text{Ir}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$ Plus Hydrogen. *J. Am. Chem. Soc.* **2017**, *139*, 5444-5457.
- ¹⁹ Özhava, D.; Özkar, S., Rhodium(0) Nanoparticles Supported on Nanosilica: Highly Active and Long Lived Catalyst in Hydrogen Generation from the Methanolysis of Ammonia Borane. *Appl. Catal. B*, **2016**, *181*, 716-726.
- ²⁰ Özkar, S.; Finke, R. G., Palladium(0) Nanoparticle Formation, Stabilization, and Mechanistic Studies: $\text{Pd}(\text{acac})_2$ as a Preferred Precursor, $[\text{Bu}_4\text{N}]_2\text{HPO}_4$ Stabilizer, Plus the Stoichiometry, Kinetics, and Minimal, 4-Step Mechanism of the Palladium Nanoparticle Formation and Subsequent Agglomeration Reactions. *Langmuir*, **2016**, *32*, 3699-3716.
- ²¹ Georgiev, P.; Bojinova, A.; Kostova, B.; Momekova, D.; Bjornholm, T.; Balashev, K., Implementing Atomic Force Microscopy (AFM) for Studying Kinetics of Gold Nanoparticle's Growth. *Colloids Surf. A*, **2013**, *434*, 154-163.
- ²² Kolbert, E.; Why Facts Don't Change Our Minds. The New Yorker, 2017, Feb 27th issue. <http://www.newyorker.com/magazine/2017/02/27/why-facts-dont-change-our-minds> (Accessed 8/28/2017.)
- ²³ Schmidt, A. F.; Smirnov, V.V., Concept of “Magic” Number Clusters as a New Approach to the Interpretation of Unusual Kinetics of the Heck Reaction With Aryl Bromide, *Top. Catal.* **2005**, *32*, 71-75.
- ²⁴ Özkar, S.; Finke, R., Dust Effects On Nucleation Kinetics and Nanoparticle Product Size-Distributions: The Illustrative Case Study of a Prototype $\text{Ir}(0)_n$ Transition-Metal Nanoparticle Formation System. *Langmuir*, **2017**, *33*, 6550-6562.
- ²⁵ Laxson, W. W.; Finke, R. G. Nucleation is Second Order: An Apparent Kinetically Effective Nucleus of Two for $\text{Ir}(0)_n$ Nanoparticle Formation from $[(1,5\text{-COD})\text{Ir}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$ Plus Hydrogen. *J. Am. Chem. Soc.* **2014**, *136*, 17601-17615.
- ²⁶ Richards, V. N.; Rath, N. P.; Buhro, W. E. Pathway from a Molecular Precursor to Silver Nanoparticles: The Prominent Role of Aggregative Growth. *Chem. Mater.* **2010**, *22*, 3556-3567.
- ²⁷ Hornstein, B. J.; Finke, R. G. Transition-Metal Nanocluster Kinetic and Mechanistic Studies Emphasizing Nanocluster Agglomeration: Demonstration of a Kinetic Method That Allows

- Monitoring of All Three Phases of Nanocluster Formation and Aging. *Chem. Mater.* **2004**, *16*, 139-150. (See also the addition / correction: *Chem. Mater.* **2004**, *16*, 3972.)
- ²⁸ Besson, C.; Finney, E. E.; Finke, R. G. A Mechanism for Transition-Metal Nanoparticle Self-Assembly. *J. Am. Chem. Soc.*, **2005**, *127*, 8179-8184.
- ²⁹ Besson, C.; Finney, E. E.; Finke, R. G. Nanocluster Nucleation, Growth, and Then Agglomeration Kinetic and Mechanistic Studies; A More General, Four-Step Mechanism Involving Double Autocatalysis. *Chem. Mater.* **2005**, *17*, 4925-4938.
- ³⁰ Finney, E. E.; Finke, R. G. The Four-Step, Double-Autocatalytic Mechanism for Transition-Metal Nanocluster Nucleation, Growth, and Then Agglomeration: Metal, Ligand, Concentration, Temperature, and Solvent Dependency Studies. *Chem. Mater.*, **2008**, *20*, 1956-1970.
- ³¹ Kent, P. D.; Mondloch, J. E.; Finke, R. G. A Four-Step Mechanism for the Formation of Supported-Nanoparticle Heterogeneous Catalysts in Contact with Solution: The Conversion of Ir(1,5-COD)Cl/g-Al₂O₃ to Ir(0)_{~170}/g-Al₂O₃. *J. Am. Chem. Soc.* **2014**, *136*, 1930-1941.
- ³² Yin, C. X.; Finke, R. G. Kinetic and Mechanistic Studies of Vanadium-Based, Extended Catalytic Lifetime Catechol Dioxygenases. *J. Am. Chem. Soc.* **2005**, *127*, 13988-13996.
- ³³ Bayram, E.; Linehan, J. C.; Fulton, J. L.; Roberts, J. A. S.; Szymczak, N. K.; Smurthwaite, T. D.; Özkaz, S.; Balasubramanian, M.; Finke, R. G. Is it Homogeneous or Heterogeneous Catalysis Derived from [RhCp*Cl₂]₂? *In Operando* XAFS, Kinetic, and Crucial Kinetic Poisoning Evidence for Subnanometer Rh₄ Cluster-Based Benzene Hydrogenation Catalysis. *J. Am. Chem. Soc.* **2011**, *133*, 18889-18902.
- ³⁴ Smith, S. E.; Sasaki, J. M.; Bergman, R. G.; Mondloch, J. E.; Finke, R. G. Platinum-Catalyzed Phenyl and Methyl Group Transfer from Tin to Iridium: Evidence for an Autocatalytic Reaction Pathway with an Unusual Preference for Methyl Transfer. *J. Am. Chem. Soc.* **2008**, *130*, 1839-1841.
- ³⁵ Mondloch, J. E.; Wang, Q.; Frenkel, A. I.; and Finke, R. G. Development Plus Kinetic and Mechanistic Studies of a Prototype Supported-Nanoparticle Heterogeneous Catalyst Formation System in Contact with Solution: Ir(1,5-COD)Cl/γ-Al₂O₃ and its Reduction by H₂ to Ir(0)_n/γ-Al₂O₃. *J. Am. Chem. Soc.* **2010**, *132*, 9701-9714.
- ³⁶ Mondloch, J. E.; Finke, R. G. Supported-Nanoparticle Heterogeneous Catalyst Formation in Contact with Solution: Kinetics and Proposed Mechanism for the Conversion of (1,5-COD)Cl/γ-Al₂O₃ to Ir(0)_{~900}/γ-Al₂O₃. *J. Am. Chem. Soc.* **2011**, *133*, 7744-7756.
- ³⁷ Mondloch, J. E.; Bayram, E.; Finke, R. G. A Review of the Kinetics and Mechanisms of Formation of Supported-Nanoparticle Heterogeneous Catalysts. *J. Mol. Catal. A.* **2012**, *355*, 1-38.
- ³⁸ Morris, A. M.; Watzky, M. A.; Agar, J. N.; Finke, R. G. Fitting Neurological Protein Aggregation Kinetic Data via a 2-Step, Minimal/"Ockham's Razor" Model: The Finke-Watzky Mechanism of Nucleation Followed by Autocatalytic Surface Growth. *Biochem.* **2008**, *47*, 2413-2427.
- ³⁹ Watzky, M. A.; Morris, A. M.; Ross, E. D.; Finke, R. G. Fitting Yeast and Mammalian Prion Aggregation Kinetic Data with the Finke-Watzky Two-Step Model of Nucleation and Autocatalytic Growth. *Biochem.* **2008**, *47*, 10790-10800.
- ⁴⁰ Morris, A. M.; Finke, R. G. α-Synuclein Aggregation Variable Temperature and Variable pH Kinetic Data: A Reanalysis Using the Finke-Watzky 2-Step Model of Nucleation and Autocatalytic Growth. *Biophys. Chem.* **2009**, *140*, 9-15.
- ⁴¹ Morris, A. M.; Watzky, M. A.; Finke, R. G. Protein Aggregation Kinetics, Mechanism, and Curve-Fitting: A Review of the Literature. *Biophys. Biochem. Acta* **2009**, *1794*, 375-397.
- ⁴² Finney, E. E.; Finke, R. G. Fitting and Interpreting Transition-Metal Nanocluster Formation and Other Sigmoidal-Appearing Kinetic Data: A More Thorough Testing of Dispersive Kinetic vs Chemical-Mechanism-Based Equations and Treatments for 4-Step Type Kinetic Data. *Chem. Mater.* **2009**, *21*, 4468-4479.

- ⁴³ Tong, F.; Hanson, M. P.; Bardeen, C. Analysis of Reaction Kinetics in the Photochemical Molecular Crystal 9-Methylanthracene Using an Extended Finke-Watzky Model. *J. Phys. Chem. Chem. Phys.* **2016**, *18*, 31936-31945.
- ⁴⁴ Avinash, M. B.; Sandeepa, K. V.; Govindaraju, T. Emergent Behaviors in Kinetically Controlled Dynamic Self-Assembly of Synthetic Molecular Systems. *ACS Omega*, **2016**, *1*, 378-387.
- ⁴⁵ Oladoja, N. A. A Critical Review of the Applicability of Avrami Fractional Kinetic Equation in Adsorption-Based Water Treatment Studies. *Desalin. Water Treat.* **2015**, *57*, 15813-15825.
- ⁴⁶ Özkar, S.; Finke, R. G. Transition-Metal Nanocluster Stabilization Fundamental Studies: Hydrogen Phosphate as a Simple, Effective, Readily Available, Robust, and Previously Unappreciated Stabilizer for Well-Formed, Isolable, and Redissolvable Ir(0) and Other Transition-Metal Nanoclusters. *Langmuir*, **2003**, *19*, 6247-6260.
- ⁴⁷ Aiken, J. D. III; Finke, R. G. Nanocluster Formation Synthetic, Kinetic, and Mechanistic Studies. The Detection of, and Then Methods to Avoid, Hydrogen Mass-Transfer Limitations in the Synthesis of Polyoxoanion- and Tetrabutylammonium-Stabilized, Near-Monodisperse 40 ± 6 Å Rh(0) Nanoclusters. *J. Am. Chem. Soc.* **1998**, *120*, 9545.
- ⁴⁸ Weddle, K. S.; Aiken, J. D. III, Finke, R. G. Rh(0) Nanoclusters in Benzene Hydrogenation Catalysis: Kinetic and Mechanistic Evidence that a Putative $[(C_8H_{17})_3NCH_3]^+[RhCl_4]^-$ Ion-Pair Catalyst is Actually a Distribution of Cl^- and $[(C_8H_{17})_3NCH_3]^+$ Stabilized Rh(0) Nanoclusters. *J. Am. Chem. Soc.* **1998**, *120*, 5653.
- ⁴⁹ Hagen, C. M.; Widegren, J. A.; Maitlis, P. M.; Finke, R. G. Is it Homogeneous or Heterogeneous Catalysis? Compelling Evidence for Both Types of Catalysts Derived from $[Rh(\eta^5-C_5Me_5)Cl_2]_2$ as a Function of Temperature and Hydrogen Pressure. *J. Am. Chem. Soc.* **2005**, *127*, 4423-4432.
- ⁵⁰ Harada, M.; Inada, Y. In Situ Time-Resolved XAFS Studies of Metal Particle Formation by Photoreduction in Polymer Solutions. *Langmuir*, **2009**, *25*, 6049-6061.
- ⁵¹ Harada, M.; Yoshihiko, K. Nucleation and Aggregative Growth Process of Platinum Nanoparticles Studied by in Situ Quick XAFS Spectroscopy. *Langmuir*, **2012**, *28*, 2415-2428.
- ⁵² Hagen, C. M.; Vieille-Petit, L.; Laurenczy, G.; Süß-Fink, G.; Finke, R. G. Supramolecular Triruthenium Cluster-Based Benzene Hydrogenation Catalysis: Fact or Fiction? *Organometallics*, **2005**, *24*, 1819-1831.
- ⁵³ LaGrow, A. P.; Ingham, B.; Toney, M. F.; Tilley, R. D. Effect of Surfactant Concentration and Aggregation on the Growth Kinetics of Nickel Nanoparticles. *J. Phys. Chem. C* **2013**, *117*, 16709-16718.
- ⁵⁴ Kytsya, A.; Bazylyak, L.; Hrynda, Y.; Horechyy, A.; Medvedevdkikh, Y. The Kinetic Rate Law for the Autocatalytic Growth of Citrate-Stabilized Silver Nanoparticles. *Int. J. Chem. Kinetics*, **2015**, *47*, 351-360.
- ⁵⁵ Harada, M.; Kizaki, S. Formation Mechanism of Gold Nanoparticles Synthesized by Photoreduction in Aqueous Ethanol Solutions of Polymers Using in Situ Quick Scanning X-ray Absorption Fine Structure and Small-Angle X-ray Scattering. *Cryst. Growth. Des.* **2016**, *16*, 1200-1212.
- ⁵⁶ Tatarchuk, V.V.; Sergievskaya, A. P.; Korda, T. M.; Druxhinina, I. A.; Zaikovsky, V. I. Kinetic Factors in the Synthesis of Silver Nanoparticles by Reduction of Ag^+ with Hydrazine in Reverse Micelles of Triton N-42. *Chem Mater.* **2013**, *25*, 3570-3579.
- ⁵⁷ Finney, E. E.; Finke, R. G. Is There a Minimal Chemical Mechanism Underlying Classical Avrami-Erofe'ev Treatments of Phase-Transformation Kinetic Data?, *Chem. Mater.* **2009**, *21*, 4692-4705.
- ⁵⁸ Ashley, B.; Vakil, P. N.; Lynch, B. B.; Dyer, C. M.; Tracey, J. B.; Owens, J.; Strouse, G. F. Microwave Enhancement of Autocatalytic Growth of Nanometals, *J. Phys Chem C*, **2017**, *11*, 9957-9967.