

Supplementary Information (SI)

Gravimetric Analysis of the Autocatalytic Growth of Copper Microparticles in Aqueous Solution

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Derivation

Derivations of Eq. (4)

In the text, the governing equation of particle growth from the aspect of total particle mass is written as Eq. (3). In order to avoid confusion surrounding this unit, dimensionless terms $\tau \left(\equiv \frac{t}{t_c} \right)$ and $\gamma \left(\equiv \frac{m}{m_f} \right)$ were introduced, and then the governing equation was converted to that below with the initial condition $\gamma = 0$ at $\tau = 0$:

$$\begin{aligned} \frac{d}{dt} \left(\frac{m}{m_f} \right) &= k_n \left(1 - \frac{m}{m_f} \right) + k_g \left(1 - \frac{m}{m_f} \right) \left(\frac{m}{m_f} \right)^{2/3} \\ \rightarrow \frac{1}{t_c} \cdot \frac{d\gamma}{d\tau} &= k_g \gamma^{2/3} (1 - \gamma) + k_n (1 - \gamma) \end{aligned} \quad (S1)$$

Substitute $\gamma = x^3$, $d\gamma = 3x^2 dx$

$$\begin{aligned} \frac{1}{t_c} \frac{dx^3}{d\tau} &= k_g x^2 (1 - x^3) + k_n (1 - x^3) \\ \frac{3x^2 dx}{k_g x^2 (1 - x^3) + k_n (1 - x^3)} &= t_c d\tau \\ \frac{3x^2 dx}{(1 - x^3)(k_g x^2 + k_n)} &= t_c d\tau \end{aligned} \quad (S2)$$

Then, Eq. (S2) was derived when integrating both sides with the initial condition and re-substitution by $x =$

$$\begin{aligned} \gamma^{1/3} &= \frac{m^{1/3}}{m_f^{1/3}}, \quad \tau = \frac{t}{t_c} \\ t &= \frac{1}{2(k_g^2 + k_n^2)} \left[(k_g - 2k_n)(k_g + k_n) \ln \left(1 - \frac{m}{m_f} \right) - 3k_g(k_g - k_n) \ln \left\{ 1 - \left(\frac{m}{m_f} \right)^{1/3} \right\} - 6k_g \sqrt{k_g k_n} \tan^{-1} \left\{ \sqrt{\frac{k_g}{k_n}} \left(\frac{m}{m_f} \right)^{1/3} \right\} + \right. \\ &\quad \left. 3k_n^2 \ln \left\{ \frac{k_g}{k_n} \left(\frac{m}{m_f} \right)^{2/3} + 1 \right\} + 2\sqrt{3}k_g(k_g + k_n) \left\{ \tan^{-1} \left(\frac{2}{\sqrt{3}} \left(\frac{m}{m_f} \right)^{1/3} + \frac{1}{\sqrt{3}} \right) - \frac{\pi}{6} \right\} \right] \end{aligned} \quad (S3)$$

In the final Eq. (S3), terms k_g and k_n are fitting parameters to define the activation energy of particle formation and growth, respectively. The above equation only focuses on particle formation and nucleation, but in real systems, there is induction time to form nuclei, which mainly consists of the relaxation time, and

some activation and nucleation time. Formaldehyde requires activation time which is the period for the conversion to methylene glycol, for reaction. Therefore, the induction time t_{ind} , was also added as a fitting parameter. Consequently, the equation for fitting to the experimental results is Eq. (S4):

$$t - t_{ind} = \frac{1}{2(k_g^2 + k_n^2)} \left[(k_g - 2k_n)(k_g + k_n) \ln \left(1 - \frac{m}{m_f} \right) - 3k_g(k_g + k_n) \ln \left\{ 1 - \left(\frac{m}{m_f} \right)^{\frac{1}{3}} \right\} - 6k_g \sqrt{k_g k_n} \tan^{-1} \left\{ \sqrt{\frac{k_g}{k_n}} \left(\frac{m}{m_f} \right)^{\frac{1}{3}} \right\} + 3k_n^2 \ln \left\{ \frac{k_g}{k_n} \left(\frac{m}{m_f} \right)^{\frac{1}{3}} + 1 \right\} + 2\sqrt{3}k_g(k_g + k_n) \left\{ \tan^{-1} \left(\frac{2}{\sqrt{3}} \left(\frac{m}{m_f} \right)^{\frac{1}{3}} + \frac{1}{\sqrt{3}} \right) - \frac{\pi}{6} \right\} \right] \quad (S4)$$

Experimental condition

- i) Substrate: Cu foil (0.8 cm × 1.0 cm)
- ii) Pretreatment: 10 vol.% H₂SO₄(95 %)+3 vol.% H₂O₂ (2 min) → D.I. rinsing (10 s) → H₂SO₄ (2 min, 95 %) (25°C)
- iii) Solution: x mM CuSO₄·5H₂O + 100 mM HCHO + 100 mM EDTA ($x = (10 - 50)$), 67°C, 0.6 M KOH, pH 13.5, stirring)
- iv) Cu film growth: (20 min preheating) pretreatment → D.I. rinsing (10 s) → 3 min dipping in the solution

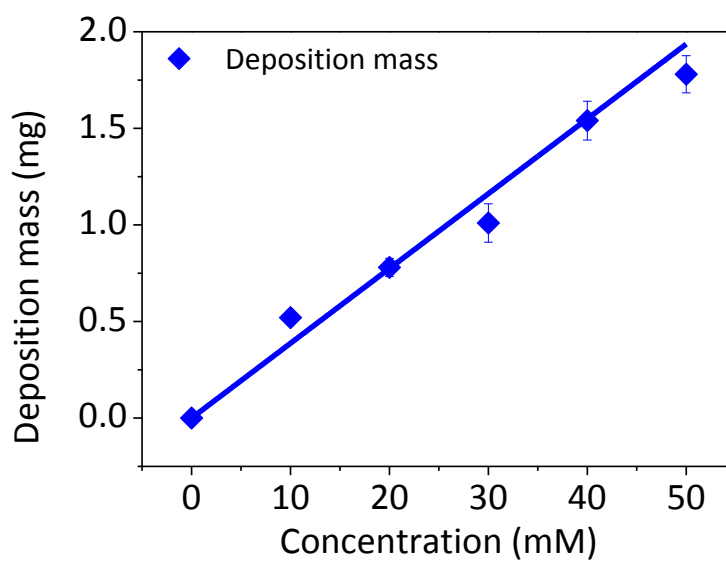
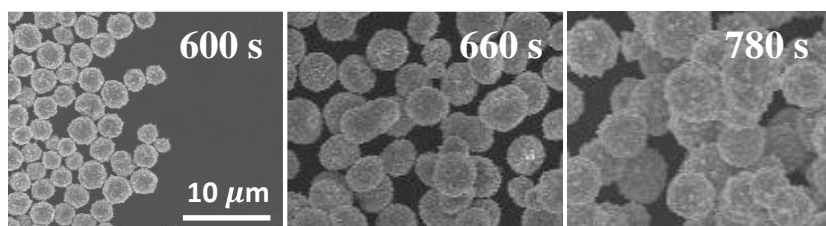
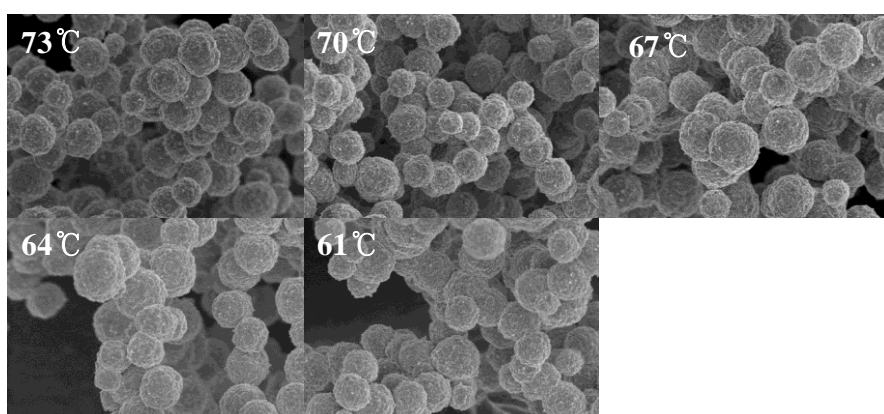


Figure S1. Cu film growth on copper foil.

(a)



(b)



(c)

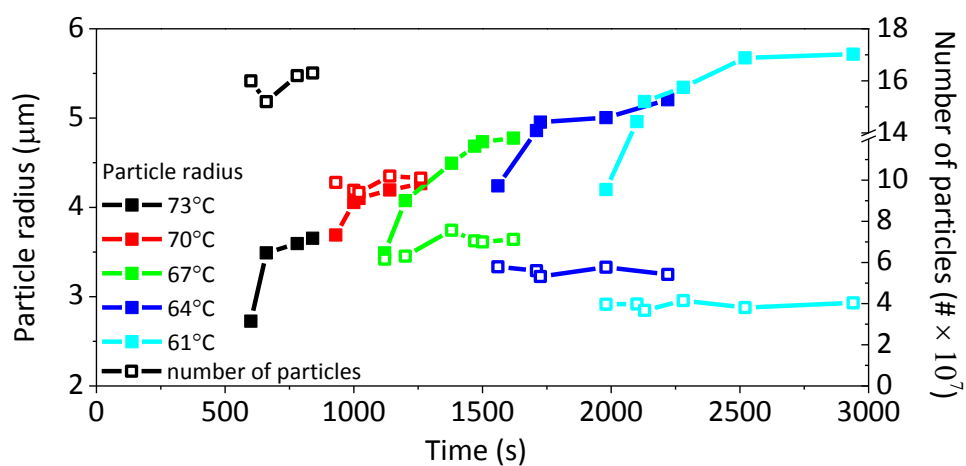
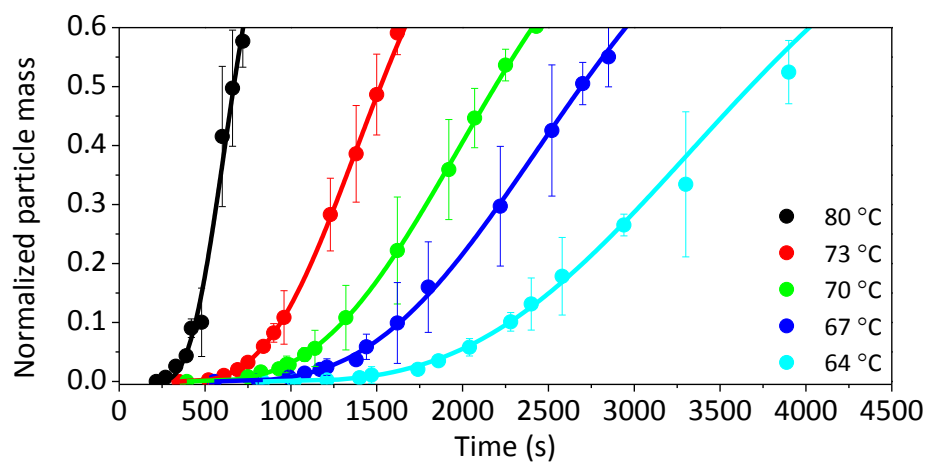


Figure S2. FESEM imagery of the synthesized Cu particle according to (a) reaction time, and (b) temperature; and (c) Number of particles and their radius variation.

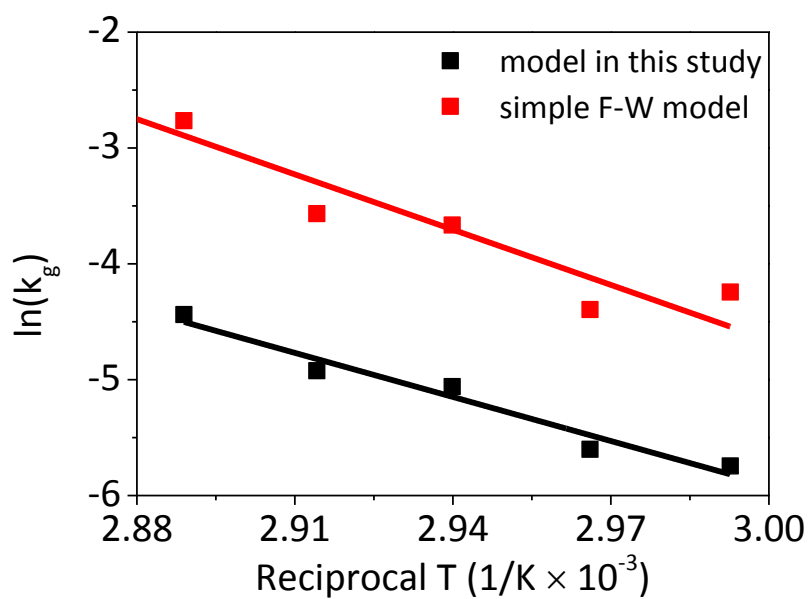
(a)



(b)

Temperature (°C)	k_g (s ⁻¹)	k_n (s ⁻¹) × 10 ⁻¹⁰	t_{ind} (s)
80	0.005789	130.3	227.1
73	0.002427	51.13	347.2
70	0.001576	24.72	380.2
67	0.001334	15.00	553.1
64	0.000902	7.28	832.5

Figure S3. In 2,2'-dipyridyl contained solution, (a) particle growth by gravimetric method. (b) Fitting parameters of the solution using Eq. (4)

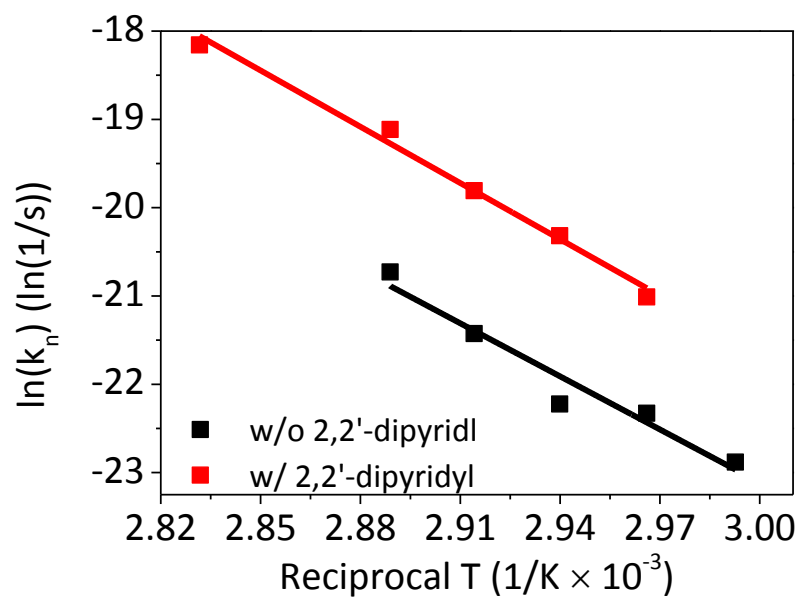


$$E_a(\text{simple F-W model}) = 137.7 \text{ kJ/mol}$$

$$E_a(\text{model in this study}) = 105.4 \text{ kJ/mol}$$

Figure S4. Estimated activation energy of Cu growth using (a) the simple Finke-Watzky model, and (b) the model in this study. Note that it is inappropriate to compare k_g values between both model directly, since k_g for the simple F-W model has a unit of [cm³/mol·s], whereas the unit of k_g for the model in this study is [s].

(a)



(b)

Temperature ($^{\circ}\text{C}$)	Average number of particles ($\#, \times 10^7$)	
	w/o 2,2'-dipyridyl	w/ 2,2'-dipyridyl
80		55.1 (± 3.5)
73	15.9 (± 0.52)	20.1 (± 1.59)
70	9.81 (± 0.34)	15.7 (± 1.36)
67	6.87 (± 0.45)	11.3 (± 0.94)
64	5.58 (± 0.21)	8.60 (± 0.19)
61	3.94 (± 0.17)	

Figure S5. (a) Arrhenius plot of k_n measured in the absence and the presence of 2,2'-dipyridyl in the solution, and (b) the average number of particles under each solution.