Supporting information for

Quantifying the Nucleation and Growth Kinetics of Microwave Nanochemistry Enabled by in-situ High-Energy X-ray Scattering

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Figure S1. Analysis of the HEXRD pattern recorded at 30 min of the microwave reaction performed at 140 °C. The HEXRD peaks were fitted with (A) the Gaussian function in origin software and (B) GSAS Rietveld refinement Software. The extracted peak area and FWHM of Ag(111) peak are very close for two fitting methods. The positions of the standard XRD peaks of Ag are also presented for reference. The difference between the calculated refinement pattern and the measured pattern is only 1.87%. Wavelength of the X-ray was 0.1771 Å.



Figure S2. GSAS Rietveld refinement of calibration HEXRD pattern of the standard LaB_6 crystalline powders. The difference between the calculated refinement pattern and the measured pattern is only 0.25%.



Figure S3. The instrumental contribution to peak broadening (δ_i) as a function of 2θ , which was calculated according to the HEXRD pattern of the standard crystalline LaB₆ powders.

Calculation of lateral dimensions of the as-grown Ag nanocrystals. By measuring and fitting the HEXRD pattern of dispersed LaB₆ powders shown in Figure S2 and Figure S3, the parameters (U, V and W) of the profile shape function were obtained.[Caglioti, G.; Paoletti, A. t.; Ricci, F. *Nuclear Instruments* **1958**, *3*, 223.] The instrumental contribution to peak broadening (δ_i) was then calibrated with the equation:

$$\delta_i = Utan^2\theta + Vtan\theta + W. \tag{S1}$$

The FWHM values (δ_m) extracted from the in-situ HEXRD patterns recorded from the colloidal Ag nanocrystals formed in the microwave synthesis were corrected with consideration of the instrumental contribution. The corrected FWHM values (δ_s) were then calculated by following the equation:

$$\delta_s = \sqrt{\delta_m^2 - \delta_i^2}.$$
 (S2)

With the corrected FWHM values, the average lateral dimensions of the Ag nanocrystals were calculated by employing the Scherrer equation:

$$L = \frac{K\lambda}{(\delta_s)\cos\theta},\tag{S3}$$

where *L* is the average crystalline size of the Ag nanocrystals, *K* is the dimensionless shape factor with a value close to 0.9 (for the peaks fitted with Gaussian function), λ is the wavelength of X-ray, δ_s is the corrected FWHM value with exclusion of the instrumental contribution (with unit in radian), and θ is the Bragg angle. For example, the HEXRD pattern recorded from the microwave reaction of Figure 1 at 30 min exhibited a FWHM of 0.01479 for the Ag(111) peak (Figure S2), while the instrumental contribution to peak broadening (δ_i) at 2 θ of 4.29° was 0.0114 (Figure S3). The FWHM was then corrected to be 0.0093 (i.e., 1.62 × 10⁻⁴ in radian) by following eq. S2. According to the Sherrer equation, the average crystalline size of the Ag nanocrystals along the <111> crystalline orientations was calculated to be 98.25 nm. **Determination of rate constant of the microwave reactions.** In generally, chemical synthesis of noble-metal nanocrystals through reduction of metal ions in a reducing solvent (for instant, reduction of Ag^+ ions in hot ethylene glycol (EG) presented in this work) can be considered as a bimolecular elementary reaction, $Ag^+ + EG \rightarrow Ag$ (product), with a reaction rate:

$$Rate = k'[Ag^+][EG].$$
(S4)

This second-order rate law follows directly from the collision theory due to involvement of collision and electron transfer between the Ag^+ ions and EG molecules. When EG is used as solvent, its concentration is essential constant throughout the reaction. As a result, the reaction rate can be simplified as that of the first-order reaction,

Rate =
$$\frac{-d[Ag^+]}{dt} = k[Ag^+],$$
 (S5)

where *k* is rate constant with the unit of s⁻¹, and $[Ag^+]$ represents the concentration of Ag^+ in reaction solution that usually equals to that of AgNO₃. Integration of both sides of the equation (S5) results

$$\ln\frac{[\mathrm{Ag^+}]_t}{[\mathrm{Ag^+}]_0} = -k\mathsf{t},\tag{S6}$$

where $[Ag^+]_t$ represents the concentration of AgNO₃ at a reaction time of *t*, while the $[Ag^+]_0$ is the initial concentration of AgNO₃ before the reaction starts.



Figure S4. Derivative of Figure 2A showing the dependence of Ag(111) peak area on the reaction time, *t*.



Figure S5. Time-dependent average lateral crystalline dimensions of the Ag nanoparticles along the Ag<200> crystalline directions.



Figure S6. TEM (left) and high-resolution TEM images (right) of the Ag nanoparticles synthesized through the microwave reaction at 140 $^{\circ}$ C for 12 min. The characterization results clearly show that the Ag seeds formed at the nucleation stage are mainly terminated by {111} facets.



Figure S7. (center) TEM image and high-resolution TEM images of a Ag nanopartilce formed throught the microwave reaction at 140 °C for 40 min. The characterization results highlight that the as-grown Ag nanoparticles are usually terminated with both {111} and {100} facets.



Figure S8. Plots of the peak area of Ag(200) peaks as a function of reaction time at different reaction temperatures. The reaction conditions are the same of Figure 3A.



Figure S9. TEM images of the Ag nanoparticles synthesized through the microwave reactions at different temperatures: (A) 140 $^{\circ}$ C, (B) 160 $^{\circ}$ C; (C) 180 $^{\circ}$ C. (D) UV-Visible absorption spectra of the as-synthesized Ag nanoparticles shown in (A-C), showing the redshift of peak position with increase of particle size.



Figure S10. Plots of the peak area of Ag(111) peaks as a function of reaction time at different $AgNO_3$ concentrations: 0.1 M, 0.2M to 0.3M. The average crystalline dimensions of the product Ag nanoparticles are also presented in the figure.



Figure S11. Plots of the peak area of Ag(111) peaks as a function of reaction time at different PVP concentrations: 0.2 M (116 nm), 0.3M (116 nm), and 0.4 M (118nm). The numbers in the brackets represent the average crystalline dimensions of the synthesized Ag nanoparticles.

Table S1. Fitted parameters of the sigmoidal functions corresponding to the Ag(111) peakarea at the different reaction temperatures.

Temperatures °C	Equation	Equation $Y = A2 + (A1-A2)/(1 + exp((x-x_0)/dx))$					
	A1	A2	X ₀	dx			
140	0	11.757	22.2204	2.84443			
160	0	11.741	9.8357	0.8172			
180	0	11.890	6.5017	0.1959			

*A1 means the value of peak area at t=0 min; A2 means the value of peak area at t=40 min; x_0 means the time when 50% Ag⁺ ions are reduced.

Table S2. Fitted parameters of the sigmoidal functions corresponding to the Ag(111) peakarea of the reactions at 160 °C with the different AgNO3 concentrations.

Temperatures °C	AgNO ₃ concentrations mol/L	Equation	Y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
		A1	A2	X ₀	dx
160	0.1	0	6.0508	9.9729	0.7535
160	0.2	0	11.741	9.8357	0.8172
160	0.3	0	18.3878	9.80528	0.886

Sampl	[[AgNO ₃]		PVP		Reactio	Reaction
e	Volum	Concentratio	Volum	Concentratio	р	n time	Temperatur
	e	n	e	n	(min)	(min)	e
	(mL)	(M)	(mL)	(M)			°C
Ag-0	3	0.2	3	0.3	6	40	120
Ag-1	3	0.2	3	0.3	6	40	130
Ag-2	3	0.2	3	0.3	6	40	140
Ag-3	3	0.2	3	0.3	6	40	160
Ag-4	3	0.2	3	0.3	6	40	180
Ag-5	3	0.1	3	0.3	6	40	160
Ag-6	3	0.3	3	0.3	6	40	160
Ag-7	3	0.2	3	0.2	6	40	160
Ag-8	3	0.2	3	0.4	6	40	160

Table S3. Detailed experimental conditions for the microwave reactions that were used forthe synthesis of Ag nanoparticles.