Supplementary Information (SI) for Nanoscale.

Supplementary Information

Entirely nitrate-free synthesis of silver nanoparticles via electrochemical synthesis-chemical reduction

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Table S1 Synthesis techniques of silver nanoparticles and their characteristics

Processes	Methods	Characteristics	Feedstocks	Pros and cons	Ref.
Physical	Evaporation-condensation	Feedstocks are decomposed or sublimated at high temperatures, and Ag NPs are synthesized during the condensation process.	Ag metal	✓Size distribution of Ag NPs is uniform. ✓Inexpensive Ag metal can be used as feedstock. ×Only nanospheres or NPs with uncontrollable morphologies can be produced when template is absent. ×High temperature results in excessive energy consumption.	[7]
	Pyrolysis		Ag compound		[8, 9]
Electrochemical	Electrolysis	Ag NPs are synthesized through precise control of the electro-deposition of Ag^+ on cathode.	Ag metal	✓The application of electrons as an “inexhaustible” reactant. ✓Inexpensive Ag metal can be used as feedstock. ×Cathodic template is required for the synthesis of multi-morphology Ag NPs. ×Alternating current is typically employed, leading to low productivity.	[10]
	Electro-deposition		Ag compound		[11]
Chemical reduction	Aqueous reduction	Ag NPs are synthesized using a weak or green-extract reductant, with the morphology controlled by additives and stabilizers.	Ag compound	✓Green-extract reduction enhance the environmental friendliness. ✓Multi-morphology Ag NPs can be synthesized by employing additives and stabilizers. ✓High productivity for Ag NPs with uniform size distribution. ✓Simple experimental setups and low energy consumption. ×$AgNO_3$ is employed as the principal compound feedstock in the process, which leads to nitrogen oxides generation or nitrate	[12]
	Solvothermal				[13]
	Hydrothermal				[14]
	Green-extract reduction				[15-18]

wastewater.

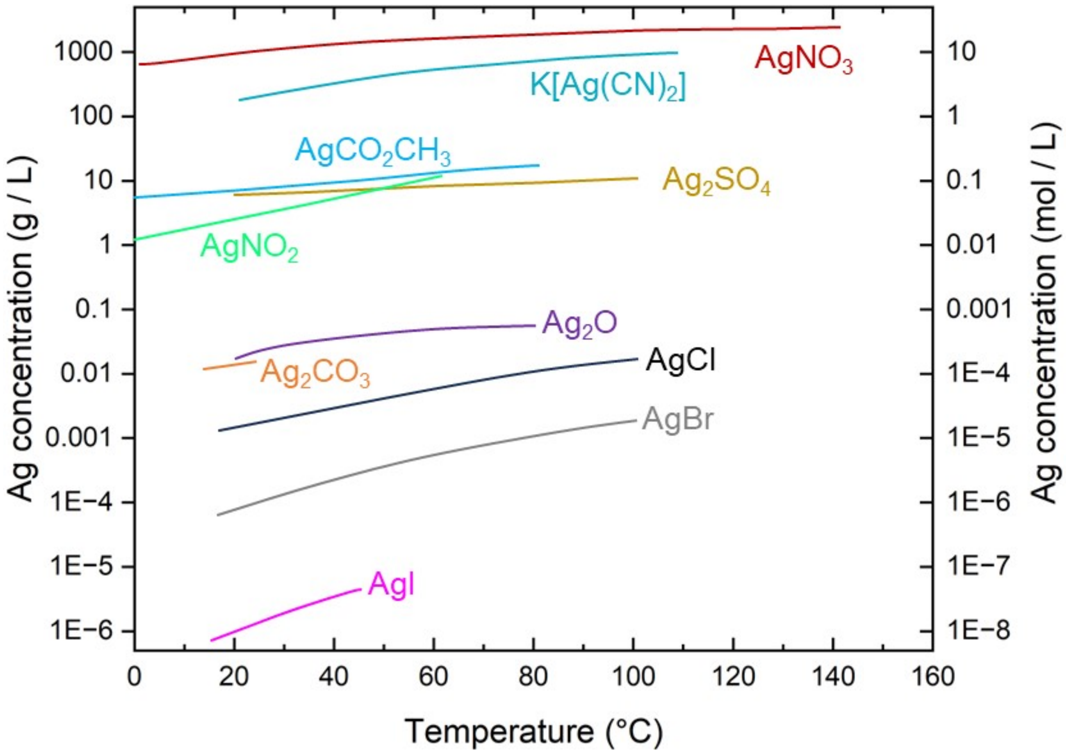

Fig. S1 Solubilities of silver compounds in water adapted from Ref. [9].

Supplementary Note 1. Material and methods

1. Materials

Analytical grade chemicals were purchased, including pure Ag sheet (99.99%), sodium acetate (CH_3CO_2Na), glacial acetic acid (CH_3CO_2H), sodium chloride (NaCl), Iron (II) sulfate heptahydrate ($FeSO_4·7H_2O$), citric acid monohydrate ($C_6H_8O_7·H_2O$), polyvinylpyrrolidone (PVP, M_w = 1300k), polyethylene glycol 600 (PEG 600), D-Glucose ($C_6H_{12}O_6$), anhydrous ethanol (C_2H_5OH), ethylene glycol ($C_2H_6O_2$), from Sinopharm Chemical Reagent Co., Ltd. without further purification. Deionized water was used throughout all experiments.

2. Electrochemical synthesis

The ES experimental setup is shown in Fig. 1. ES was conducted in a 100+100 mL H-shape cell. The electrolyte concentrations were equal in both anolyte and catholyte. A commercially available AEM, comprising a polyethylene matrix with quaternary ammonium cationic groups, was purchased from Hangzhou Huamo Technology Co., Ltd. Prior to use, the AEM was immersed in a 0.1 M aqueous solution with specific electrolyte for at least 24 hours. All electrodes underwent sandpaper polishing and ultrasonic cleaning. The metallic Ag anodes were encased in filter paper to prevent anodic slime from contaminating the anolyte. Heating and agitation were applied to the anolyte during ES process. Pt served as the cathode, where the H_2 evolution reaction occurs.

3. Chemical reduction

After ES, the anolyte was analyzed and then mixed with additives and stabilizers to produce precursor for CR. For the wet chemical reduction, the precursor mixes with the reductant rapidly under magnetic stirring. For the hydrothermal and solvothermal reductions, the precursor mixes with the reductant and solvent, and the mixture is subsequently heated in an autoclave or an oil bath. The as-synthesized Ag NPs are collected by centrifugation and are then cleaned three times, respectively, with deionized water and ethanol.

4. Instrumentation and analytical conditions

Electrochemical analyses were performed using a three-electrode electrochemical workstation (METROHM, AUTOLAB PGSTAT302N) in a 20+20 mL H-shape cell. The working electrode (WE) and the reference electrode (RE) were always in the same half-cell, while the counter electrode (CE) was in the other half-cell. A saturated calomel electrode (SCE) served as the RE, and the SCE was connected to the solution via a salt bridge filled with an electrolyte-saturated solution. The morphologies of the Ag NPs were characterized by scanning electron microscope (SEM, JEOL, JSM-IT700HR). Chemical compositions of the solutions were analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES, THERMO FISHER, iCAP PRO). Phase compositions were evaluated by X-ray diffraction (XRD, PANALYTICAL, Empyren, Cu-Kα radiation). The pH of catholyte was measured using a pH meter (LEICI, PHB-25).

Supplementary Note 2. Estimation of the Ag^+ enrichment rate in the anolyte (η_{Ag})

The η_{Ag} is estimated according to Eq. (S1), where $w_{Calc.}$ and w_A represent the calculated and measured Ag^+ concentrations (ppm) in anolyte after ES, respectively.

$$\eta_{Ag} = \frac{w_A}{w_{Calc.}} \times 100\% \qquad (S1)$$

The $w_{Calc.}$ is determined by Eq. (S2) based on Faraday's laws.

$$w_{Calc.} = \frac{Q \cdot M_{Ag.} \cdot 10^6}{F \cdot N_A \cdot m_{sol.}} \qquad (S2)$$

Where Q is the charge recorded by the coulombmeter, M_{Ag} is the relative atomic mass of Ag. F is the Faraday constant, N_A is the avogadro constant, and $m_{sol.}$ is the anolyte mass.

The w_A is determined by measuring the Ag^+ concentration in anolyte using ICP-OES, each sample is measured three times, the average value is used.

Table S2 Parameters and results of charging and discharging experiments for evaluating the enhancement in anodic dissolution of Ag.

Exp. #	Temperature (°C)	Stirring (rpm)[a]	Pulsed current (Hz)	Absolute value of discharged charge (C)	Chage ratio (%)[b]
T-1	25	0	Direct current	0.491	81.83
T-2	30			0.488	81.33
T-3	40			0.423	70.50
T-4	60			0.292	48.67
T-5	80			0.083	13.83
S-1	25	300		0.459	76.50
S-2		600		0.418	69.67
S-3		900		0.357	59.50
S-4		1200		0.318	53.00
P-1		0	0.05	0.475	79.17
P-2			0.5	0.457	76.17
P-3			5	0.468	78.00
P-4			50	0.470	78.33

[a] Stirred by magneton.

[b] The ratio of the discharged charge to the charged charge (0.60 C). A higher value indicates a more amount of CH_3CO_2Ag on the surface of the Ag electrode.

Table S3 Experimental parameters and analytical results for determining silver ion enrichment rate in the anolyte

Exp. #	Electrolysis conditions[a]	Temp. (°C)	Average voltage (V)	Starting and ending pH of catholyte[b]	CH_3CO_2Na conc. (M)	Catholyte Ag^+ conc. (ppm)[c]	$w_{Calc.}$ (ppm)[d]	w_A (ppm)[d]	η_{Ag} (%)[d]
ES-1	3 mA for 12 hours	45	3.06	3.22 to 3.47	0.10	23.24	7164.14	6649.75	92.82
ES-2		25	4.91[e]	3.15 to 3.41	0.10	27.59	7211.62	4583.71	63.56
ES-3		45	9.66	3.18 to 3.42	0.02[f]	61.47	7172.22	6363.19	88.72
ES-4		45	3.14	8.01 to 12.28[g]	0.10	NA[h]	7208.95	4018.99	55.75
ES-5		80	2.05	3.20 to 3.38	0.10	49.11	7198.27	5987.52	83.18

[a] An Ag sheet (0.2×1.0×1.5 cm) was used as the anode. The CH_3CO_2Na concentration and volume (both 20 mL) of the anolyte and the catholyte were equal. The anolyte was stirred at 900 rpm (When the agitation is too intense, the liquid surface becomes unstable).

[b] Adjusting by pure acetic acid. The increase in $CH_3CO_2^-$ concentration caused by the addition of acetic acid is assumed to be small, due to the incomplete ionization of acetic acid.

[c] Analyzed by ICP-OES, each sample was measured three times, the average value is shown.

[d] Noted in Supplementary Note 2.

[e] A voltage surge was caused by the crystallization of CH_3CO_2Ag, as shown in Fig S2(B).

[f] The CH_3CO_2Na concentration was decreased to 0.02 M to achieve the higher voltage.

[g] Catholyte pH was not adjusted.

[h] Not analyzed.

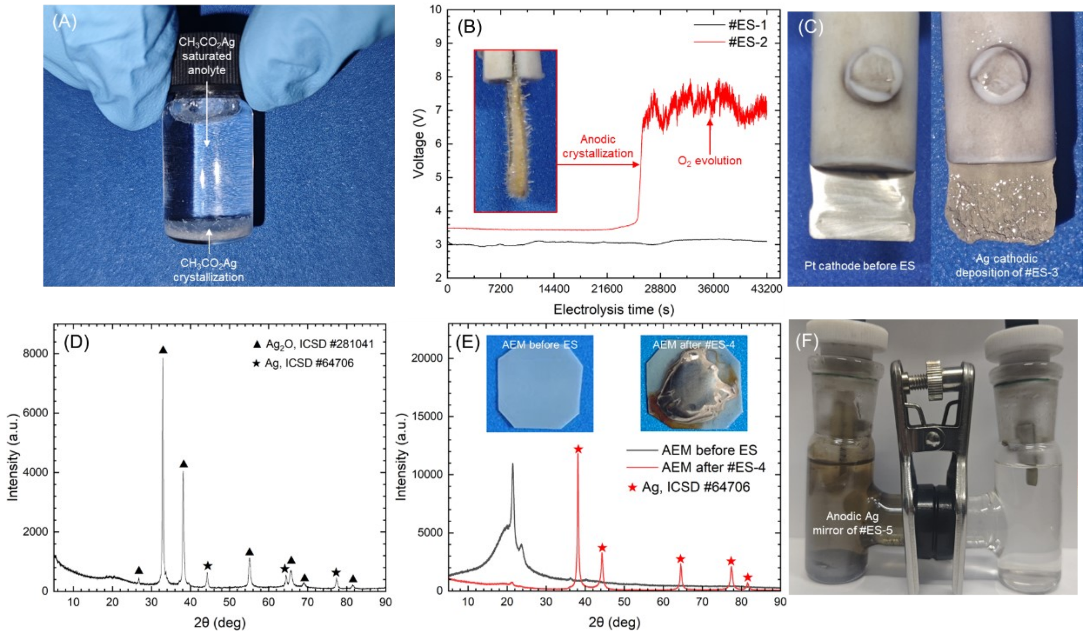

Fig. S2 Experimental phenomena revealing the factors influencing the η_{Ag}, related to the context depicted in Fig. 3. (A) CH_3CO_2Ag-saturated anolyte prepared by #ES-1. (B) Voltage changes of #ES-1 and #ES-2, embedded photograph revealing the anodic crystallization of CH_3CO_2Ag. (C) Pt cathode before and after #ES-3. (D) XRD pattern of the anolyte precipitates generated in #ES-4. (E) XRD pattern of AEM before and after #ES-4. (F) Anodic Ag mirror formation in #ES-5

Table S4 Chemical reduction parameters for synthesized silver nanoparticles from anolyte prepared by electrochemical synthesis

Exp. #	Ag^+ conc. (mM), volume of precursor (mL)[a]	Additives, their conc. in precursor (mM)	Reductant, its conc. (mM), volume (mL)	Synthesis conditions	Morphologies	Ref.
CR-1	58.72, 20	$C_6H_8O_7$, 7.11	$FeSO_4$, 143.91, 20	Room temperature, 15 min[b]	Laminar nanoflakes, Fig. 5(A)	[12]
CR-2	10.02, 50[c]	PVP, 80.05	Pure PEG 600, 40 mL	Heating in a Teflon-sealed autoclave, 260 °C, 24 h	Nanospheres, Fig. 5(B)	[13]
CR-3	50.08, 10	PVP, 78.03	Pure $C_2H_6O_2$, 5 mL	160 °C, 15 min[d]	Flocculent NPs., Fig. 5(C)	[43]
CR-4	7.52, 20[c]	PVP, 225.22; NaCl, 15.03	$C_6H_{12}O_6$, 16.72 (conc. in precursor)	Heating in a Teflon-sealed autoclave, 160 °C, 22 h	Nanowires interspersed with nanospheres, Fig. 5(D)	[14]

[a] Galvanostatic ES was conducted in a 100+100 mL H-shape cell, A current of 15 mA was applied for 12 hours at a temperature of 45 °C and an agitation speed of 900 rpm. The CH_3CO_2Na concentration was 0.1 M. The catholyte pH was maintained in 3.19-3.38, and the average voltage was 3.25 V. The Ag^+ concentration in the was 61.73 mM (6606.76 ppm), and the η_{Ag} was 92.04%. The obtained anolyte was diluted with deionized water to achieve a specific target Ag^+ concentration.

[b] The precursor solution was stirred magnetically, and the reductant solution was rapidly poured into the precursor solution.

[c] The additives and reductants were mixed with the precursor, the values represent the concentration and volume of the mixed solution.

[d] $C_2H_6O_2$ is pre-heated to 160 °C for 30min, and the precursor solution is injected drop-wise by a syringe pump into the $C_2H_6O_2$.

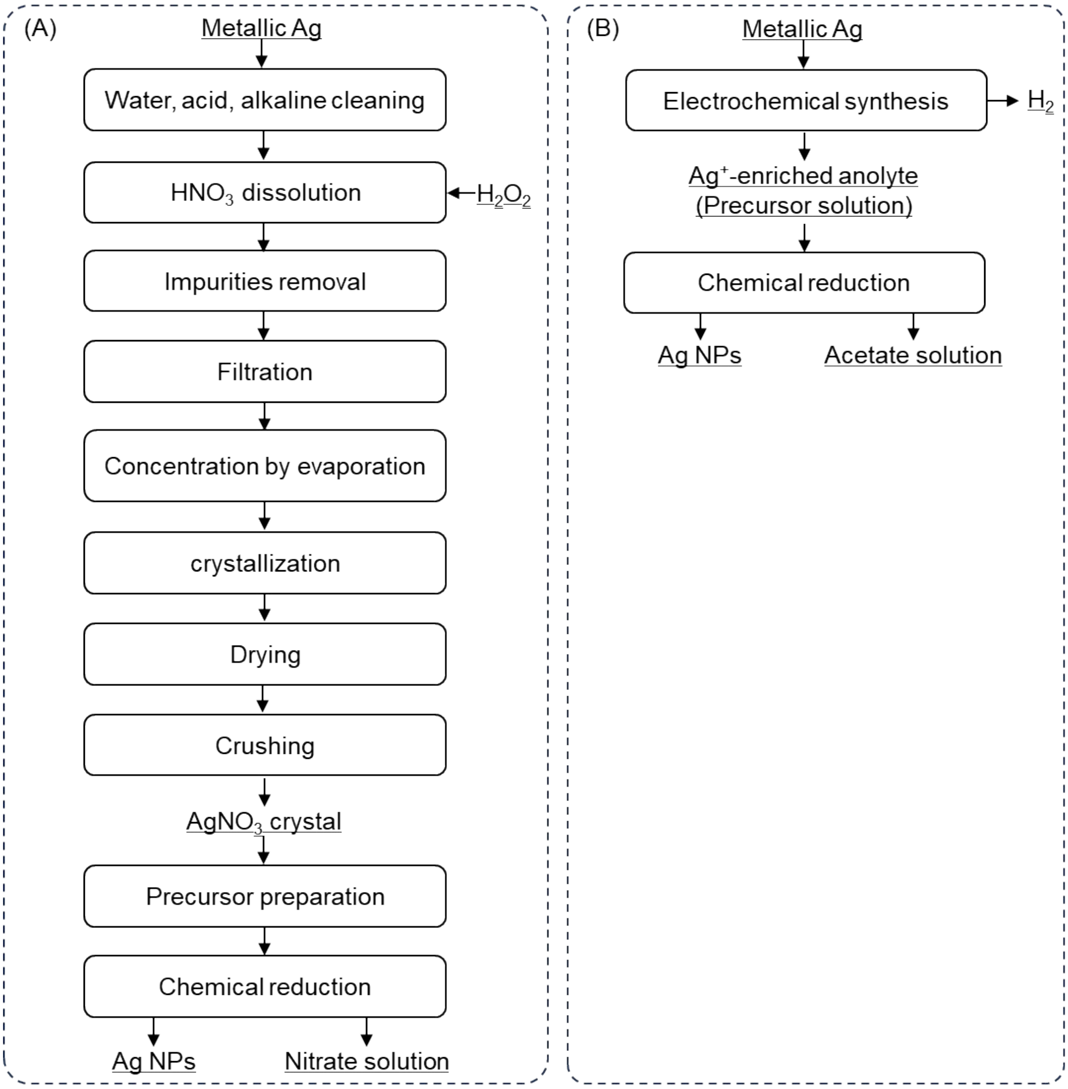

Fig. S3 Comparative workflows for Ag NPs synthesis utilizing metallic Ag as the starting material. (A) Conventional $AgNO_3$-based chemical reduction method: $AgNO_3$ production involves multiple steps (industrial scale), leading to lengthy processes that require 1-2 days for completion[23]. Additionally, extra hydrogen peroxide is needed to suppress the generation of nitrogen oxides[22]. (B) Electrochemical synthesis-chemical reduction process in this study: The process only requires two steps (laboratory scale). The precursor solution of chemical reduction can be directly prepared from metallic Ag in acetate system, and hydrogen gas is generated as a byproduct.