

Article

Process Optimization and Quality Control of a Combined Impurity Removal–Crystallization Process: Preparation of High-Purity Silver Nitrate for Photovoltaic Back Silver Applications

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Abstract

The printing adaptability and sintering compactness of photovoltaic back silver paste are highly dependent on the physical properties of the silver powder, such as tap density and particle size distribution, which in turn are directly influenced by the purity of the precursor silver nitrate. When using 4N silver ingots as the raw material, trace impurities such as Nb, Fe, Cu, and Pb remaining in the crude solution can seriously interfere with the uniform nucleation and growth of silver crystallites, leading to decreased tap density and broadened particle size distribution. This paper presents a combined impurity removal–crystallization process integrating an adsorbent with controlled evaporative crystallization. Under optimized conditions, the concentrations of Nb, Fe, Cu, and Pb impurities decreased from 44, 21, 16, and 12 ppm to below 4 ppm, respectively. Meanwhile, the controlled crystallization step further enhanced the purity of the silver nitrate crystals through the redistribution of impurities between the solid and liquid phases. When the high-purity silver nitrate prepared by this process was used to produce photovoltaic back silver powder, the tap density of the resulting silver powder increased from 2.5 g cm^{−3} to 3.4 g cm^{−3}, accompanied by a smooth surface morphology. Thermogravimetric (TG) analysis further confirmed a lower residual organic content on the particle surface. These comprehensive improvements in powder properties demonstrate the effectiveness of the proposed process in producing high-quality silver powder for photovoltaic back silver applications.

Keywords: silver nitrate; impurity removal; crystallization; process optimization; back silver



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1. Introduction

Photovoltaic power generation, as one of the most promising renewable energy technologies, has long been driven by the dual objectives of cost reduction and efficiency improvement [1]. In crystalline silicon solar cells, silver paste serves as the key conductive material for fabricating both front and back electrodes, and its performance directly determines the photoelectric conversion efficiency and long-term operational reliability

of the device [2,3]. Among these, the back silver electrode not only fulfills the function of current collection, but also plays a critical role in the soldering adhesion and long-term stability of the cell. The performance of silver paste is fundamentally governed by the physical properties of its core component, silver powder—including tap density, particle size distribution, morphology, and sintering activity—which are in turn highly dependent on the purity of the silver nitrate precursor [4]. Industrially, silver nitrate is typically produced using 4N silver ingots ($\text{Ag} \geq 99.99\%$) as the raw material. However, trace impurities at the ppm level, such as Nb, Fe, Cu, and Pb, present in the ingots can be carried over into the silver nitrate solution and subsequently enter the downstream silver powder production process. Studies have shown that these trace impurities seriously interfere with the uniform nucleation and growth of silver crystallites during the liquid-phase reduction process, resulting in poor sphericity, a broadened particle size distribution, and reduced tap density of the resulting silver powder [5,6]. Specifically, impurity ions such as Fe^{3+} and Cu^{2+} can adsorb onto the surface of initially formed silver nuclei, altering the surface energy and disrupting the isotropic growth of crystal facets. These powder deficiencies ultimately lead to deteriorated printability of the back silver paste and a porous, loosely structured electrode after sintering. Therefore, developing an efficient and controllable purification process for silver nitrate, which guarantees silver powder quality at the source, is of considerable engineering significance for enhancing the performance of photovoltaic back silver electrodes [7].

As photovoltaic cell technologies continue to evolve toward higher efficiency, silver paste, as the core material governing electrode performance, has imposed increasingly stringent requirements on the purity of its silver nitrate precursor [8,9]. To meet the growing demand for high-purity silver nitrate in the photovoltaic industry, researchers have developed various purification processes. Currently, the most commonly used methods fall into three main categories: recrystallization, chemical precipitation, and adsorption [10]. The recrystallization method achieves purification by exploiting the difference in impurity partition coefficients between the solid and liquid phases. This method offers the advantages of simple operation and good controllability. However, it exhibits poor selectivity for impurities such as Cu and Fe, whose partition coefficients are close to that of silver, and therefore requires multiple cycles to achieve high purity. This leads to a significantly reduced direct silver recovery rate, increased energy consumption, and larger volumes of wastewater discharge [11]. The chemical precipitation method selectively removes specific impurities by adding anionic precipitants. It offers the advantage of high impurity removal efficiency. However, it is prone to introducing new anionic impurities into the system, which can adversely affect the subsequent silver powder reduction process [12]. The adsorption method utilizes activated carbon, chelating resins, or porous materials to selectively capture impurity ions. It features the advantages of simple operation, environmental friendliness, and low cost. However, a single adsorption step often struggles to simultaneously achieve high removal efficiency for multiple impurity species, and the selectivity and saturation capacity of adsorbents still require further improvement [13].

To address the limitations of the aforementioned single purification methods, this paper proposes a combined purification strategy integrating adsorbent-based impurity removal with controlled evaporative crystallization. The core concept of this strategy lies in dividing the purification process into two synergistic stages. In the first stage, the adsorbent removes the majority of heavy metal impurities, such as Nb, Fe, Cu, and Pb, from the solution. In the second stage, key parameters of the evaporative crystallization process, including the crystallization yield and cooling rate, are precisely regulated. By exploiting the partition behavior of impurities between the solid and liquid phases, residual metal impurities are concentrated into the mother liquor, thereby achieving a stepwise

deep purification of the silver nitrate precursor. Compared with existing studies, the main distinguishing features of this work are as follows. (1) Adsorptive impurity removal and controlled crystallization are integrated and optimized as a systematic process, rather than being investigated as isolated unit operations. (2) The process evaluation criteria are extended from solution purity alone to the downstream application performance of the resulting silver powder, thereby establishing a full-chain quality assessment framework that spans from raw material to final application.

This study systematically investigated the effects of adsorbent dosage, adsorption time, and adsorption temperature on the removal efficiency of Nb, Fe, Cu, and Pb from the silver nitrate solution. Furthermore, the influence of parameters such as crystallization yield and cooling rate on impurity removal efficiency was explored. The high-purity silver nitrate prepared under the optimized process conditions was subsequently used to synthesize photovoltaic back silver powder. By comparing the tap density, particle size distribution, morphology, and thermogravimetric behavior of the silver powders derived from unpurified and purified silver nitrate, the practical improvements in the physical properties of the downstream silver powder achieved by this combined process were validated.

2. Materials and Methods

2.1. Experimental Materials

The raw materials included 4N silver ingots, nitric acid, silver nitrate, sodium hydroxide, activated carbon, rosin, triethanolamine, and gelatin. All chemical reagents were of analytical grade. Detailed information for each reagent is provided in the Supplementary Materials, Table S1. The main elemental composition of the 4N silver ingot was determined by ICP-MS as shown in Table 1.

Table 1. Main elemental composition of the 4N silver ingot.

Elemental	Ag	Nb	Fe	Cu	Pb	Au
Content (%)	99.99	0.0045	0.0022	0.0017	0.0014	0.0001

Determined by ICP-MS.

2.2. Preparation of the Adsorbent

Under stirring at 25 °C, 250 mL of NaOH solution (2 mol L^{−1}) was pumped into 500 mL of AgNO₃ solution (200 g L^{−1}) at a rate of 100 mL/min, and the reaction was continued for another 30 min. The resulting Ag₂O precipitate was collected by filtration, washed with deionized water until the washing solution became neutral, and dried under vacuum at 60 °C to obtain the silver oxide powder. The as-prepared silver oxide was characterized by X-ray diffraction and scanning electron microscopy, and the corresponding results are presented in Figure S1. The XRD pattern confirmed the formation of crystalline Ag₂O, and the SEM image revealed the morphology of the Ag₂O particles. Subsequently, 200 g of the above Ag₂O was mixed with 200 g of activated carbon at a mass ratio of 1:1, and the mixture was thoroughly ground in a mortar to yield the adsorbent, designated as AC-1.

2.3. Preparation of Silver Nitrate

First, 500 g of silver ingot was placed in 500 mL of nitric acid solution (30 wt%) and dissolved under continuous stirring at 70 °C. After the majority of the silver ingot had dissolved, the solution was filtered to remove any undissolved residue and then cooled to room temperature. The prepared adsorbent AC-1 was then added to the crude silver nitrate solution at a dosage of 4 g per 100 mL of solution, and the mixture was kept at 40 °C for 2 h under constant stirring for adsorption. The resulting solution was then filtered through

a 0.45 μm microporous membrane to separate the spent adsorbent. Subsequently, the purified silver nitrate solution was subjected to water-bath evaporative crystallization. A 500 mL portion of the treated solution was evaporated at 85 $^{\circ}\text{C}$ for approximately 3 h. After stopping the heating, the solution was allowed to cool under stirring for crystallization. The obtained silver nitrate crystals were collected by filtration and dried in a vacuum oven at 60 $^{\circ}\text{C}$ to yield the high-purity silver nitrate crystals. The schematic diagram of the preparation process is shown in Figure 1.

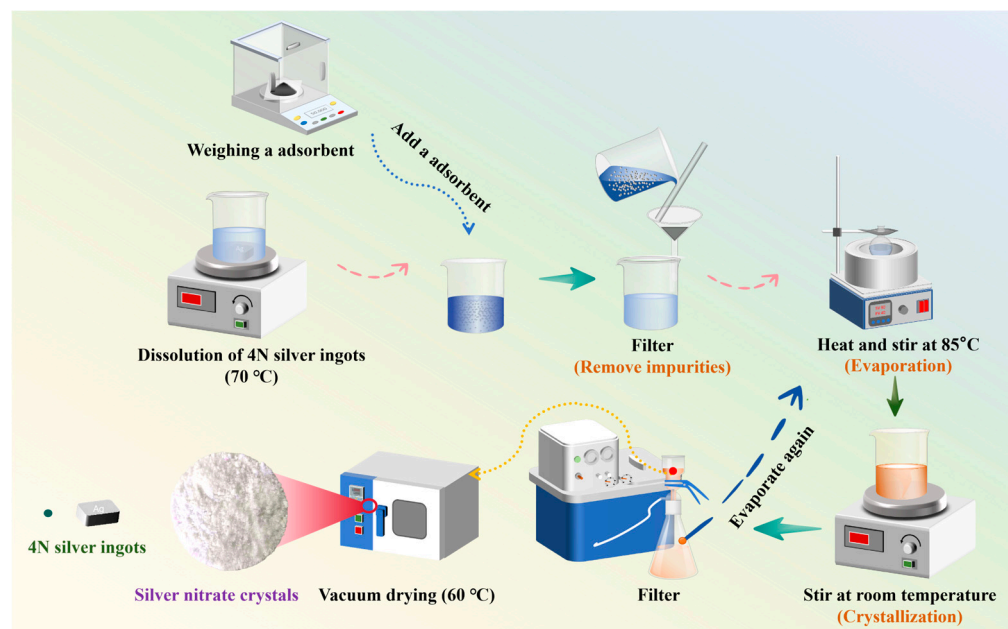


Figure 1. Schematic diagram of the silver nitrate preparation process.

2.4. Preparation of Back Silver Powder

A 100 mL portion of 200 g/L AgNO_3 solution was measured, and 50 mL of 200 g/L NaOH solution was slowly added under stirring until precipitation was complete. The mixture was stirred at 25 $^{\circ}\text{C}$ for 30 min to generate Ag_2O precipitate. The resulting precipitate was washed three times with deionized water, and then 200 mL of deionized water was added to form a Ag_2O slurry, which served as the silver source for the subsequent reduction reaction. To the above Ag_2O slurry, 0.9 mL of 60 g/L gelatin solution and 1.1 mL of 120 g/L rosin solution were added successively. The dispersion was carried out at 40 $^{\circ}\text{C}$ and 1000 r/min for 30 min. After dispersion, the system was heated to 80 $^{\circ}\text{C}$. Under continuous stirring at 1000 r/min, 1.91 g of triethanolamine reductant solution was added dropwise using a peristaltic pump. After the addition was complete, the reaction was maintained at the same temperature for another 40 min. Following the reaction, the resulting silver powder was collected by filtration and washed three times with deionized water and three times with anhydrous ethanol. The filter cake was dried in a vacuum oven at 45 $^{\circ}\text{C}$ under a vacuum of -0.04 MPa. The dried powder was passed through a 500-mesh sieve prior to subsequent characterization and performance testing.

2.5. Characterization

The Brunauer–Emmett–Teller (BET, Sibata SA-1100) specific surface area of the synthesized silver powder was determined by nitrogen adsorption at liquid nitrogen temperature on a surface area analyzer. A scanning electron microscope (SEM, VEGA COMPACT) was used to characterize the surface morphology of the product at an accelerating voltage of 15 kV. A laser particle size analyzer (Marvin APA2000) was used to measure the D_{50} of the silver powder by laser diffraction, and the measurement was repeated three times.

to obtain the average value. The tapped density was measured by the Dandong Haoyu HYL-101 bulk density tester with 3000 taps per test. A known mass of powder was placed in a graduated cylinder, and the tap density was calculated from the mass and the tapped volume. Each test was repeated three times, and the average value is reported. The X-ray diffraction (XRD, Rigaku D/MAX-2600) was used to examine the crystal structure of the sample with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over a scan range of $10\text{--}80^\circ$ at a scan rate of 2° min^{-1} . A thermogravimetric analyzer (TGA, NETZSCH) was used to determine the relationship between the sample mass and temperature. Inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7800) was employed to determine the elemental composition of the prepared high purity silver nitrate. Multi-element standard solutions were used for external calibration, and the correlation coefficients (R^2) exceeded 0.999 for all analytes. Each sample was analyzed in triplicate, and the relative standard deviation (RSD) was below 5% for all reported elements.

3. Results

3.1. Analysis of the Silver Ingot Dissolution Process

The dissolution efficiency of silver ingots directly determines the production capacity and cost of the subsequent silver nitrate preparation. During the dissolution experiment, it was observed that at 1 h of reaction, a vigorous reaction occurred in the system, with a large amount of reddish-brown gas evolving and the solution appearing pale green. The reddish-brown gas evolved during the silver dissolution process is nitrogen oxide produced from the reduction of nitric acid. The generated NO $_x$ was subsequently treated by a multi-stage absorption system. By 2 h, the gas evolution had significantly diminished, the majority of the silver ingot had dissolved, and the solution gradually clarified. After 3 h of reaction, a small amount of undissolved silver residue remained. At this point, a supplementary addition of a small volume of HNO $_3$ solution was made, and the residual silver began to dissolve slowly again, accompanied by the generation of a small amount of brown gas. By 3.5 h, the silver ingot was completely dissolved, and the solution became clear and transparent. The experimental results demonstrate that this process can effectively avoid the risk of material overflow caused by excessively vigorous reactions while ensuring a sufficient dissolution rate. Furthermore, continuous stirring was maintained throughout the dissolution process to overcome the diffusion rate limitation of Ag $^+$ in the solution and to promote the ion diffusion kinetics on the surface of the silver ingot. As the reaction proceeded, the dissolution rate exhibited a declining trend, which is primarily attributed to the continuous consumption of free HNO $_3$ in the system and the common ion effect caused by the increasing AgNO $_3$ concentration. To address the issue of the slowdown in the dissolution rate at the later stage, measures such as appropriately increasing the stirring speed, raising the reaction temperature, or adding nitric acid in multiple batches can be adopted, thereby enabling the efficient preparation of the silver nitrate solution.

During the reaction between the silver ingot and nitric acid, a large amount of NO $_x$ gas is released, which requires centralized absorption treatment to avoid environmental pollution. The treatment process flow of the nitrogen oxide gases generated during the dissolution of the silver ingot is shown in Figure 2. The tail gas was treated by absorption in a two-stage alkaline absorption tank, and the resulting absorption solution was further processed by evaporative crystallization to prepare a by-product. As shown in Figure S2, the XRD pattern of the by-product confirmed it to be a mixture of NaNO $_2$ and NaNO $_3$, indicating that the nitrogen oxides were effectively converted into useful sodium salts through the alkaline absorption process.

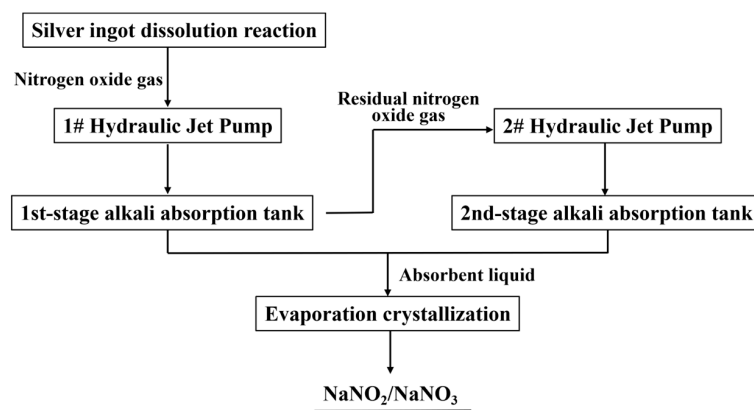


Figure 2. Schematic diagram of the nitrogen oxide gas treatment process.

3.2. Study of the Silver Nitrate Purification Process

3.2.1. Effect of Adsorbent Dosage on Impurity Content

To determine the optimal dosage of AC-1, the effect of different AC-1 additions on the removal efficiency of Nb, Fe, Cu, and Pb impurities in the silver nitrate solution was investigated under constant adsorption temperature and time. The results are shown in Figure 3a. The purification of the solution by AC-1 was achieved through the following two synergistic steps. First, the Ag_2O component in AC-1 reacted with the residual free acid in the solution through a neutralization reaction, causing the pH of the system to gradually increase from approximately 2.1 to 3.3. As the pH rose, some impurity ions in the solution (such as Fe^{3+} and Cu^{2+}) underwent hydrolysis to form hydroxide precipitates that separated from the liquid phase, achieving preliminary impurity removal. When the pH of the system stabilized at approximately 3.3, the process of removing impurities in the form of hydroxide precipitates essentially reached equilibrium. Thereafter, the remaining Ag_2O and activated carbon components in the system further captured the residual impurity ions in the solution through surface adsorption, completing the deep purification. With increasing AC-1 dosage, the content of each impurity element in the solution exhibited a downward trend. This trend can be attributed to the increased availability of active adsorption sites and the progressive rise in pH from approximately 2.1 to 3.3 caused by the Ag_2O component in AC-1, which promotes the hydrolysis and precipitation of metal ions. When the AC-1 dosage reached 4 g (i.e., 4 g per 100 mL of solution), the residual concentrations of Nb, Fe, Cu, and Pb in the silver nitrate solution all decreased to below 4 ppm, indicating that this dosage was sufficient to meet the requirements for deep impurity removal.

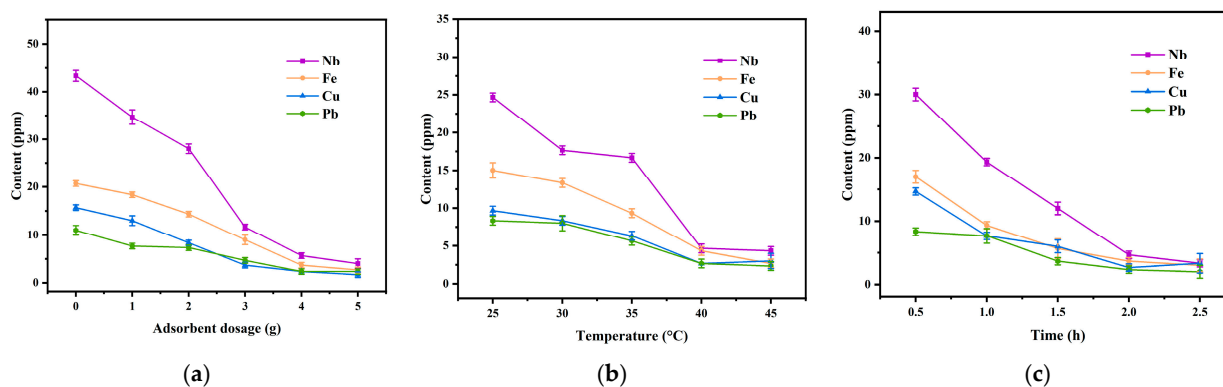


Figure 3. Results of the single-factor experiments for silver nitrate purification. (a) Effect of adsorbent dosage (adsorption temperature: 40 °C, adsorption time: 2 h); (b) Effect of adsorption temperature (adsorbent dosage: 4 g/100 mL, adsorption time: 2 h); (c) Effect of adsorption time (adsorbent dosage: 4 g/100 mL, adsorption temperature: 40 °C).

3.2.2. Effect of Adsorption Temperature on Impurity Content

Under the conditions of fixed AC-1 dosage and adsorption time, the effect of adsorption temperature on impurity removal was investigated. The experimental results are shown in Figure 3b. The adsorption temperature exerted a certain influence on impurity removal, but the degree of response varied among different impurity elements. For Cu and Pb, owing to their low initial contents, the removal efficiency exhibited only minor variations across the investigated temperature range, and their residual levels remained consistently low. In contrast, Nb displayed a more pronounced response to the adsorption temperature. A notable improvement was observed between 30 and 40 °C, suggesting that a minimum thermal energy threshold is required to overcome the activation barrier for Nb removal. As the adsorption temperature increased, the Nb removal efficiency gradually improved; when the temperature reached 40 °C, its residual concentration decreased markedly. This indicates that moderate heating can accelerate the mass transfer and diffusion of Nb ions toward the AC-1 surface and promote their chemical interaction with the active sites on the adsorbent, thereby strengthening the impurity removal effect. The pronounced temperature sensitivity of Nb removal may be attributed to the tendency of Nb to hydrolyze and form polynuclear species as the pH increases during AC-1 treatment. These polynuclear species are more readily captured by the adsorbent through electrostatic attraction and surface complexation, and their formation is accelerated at elevated temperatures. In contrast, Fe^{3+} and Cu^{2+} are predominantly removed as simple hydroxide precipitates, consistent with their weaker temperature dependence. Taking both impurity removal efficiency and engineering economy into consideration, an excessively high operating temperature would lead to increased energy consumption and a heightened risk of equipment corrosion. Therefore, 40 °C was selected as the optimal adsorption temperature. In actual production, this temperature can be flexibly fine-tuned according to the specific contents of impurity elements present in the raw material solution.

3.2.3. Effect of Adsorption Time on Impurity Content

Under the conditions of fixed AC-1 dosage and adsorption temperature, the effect of adsorption time on impurity removal was investigated. The results are shown in Figure 3c. As the adsorption time was extended, the content of each impurity element in the solution exhibited a gradual downward trend, indicating that prolonged adsorption time facilitates the thorough removal of impurities. Meanwhile, the pH of the system also rose progressively with increasing adsorption time, which is consistent with the continuous consumption of residual acid by the Ag_2O component in AC-1 and the promotion of impurity hydrolysis and precipitation. When the adsorption time reached 2 h, the content of each impurity element had decreased to its lowest level. Therefore, the optimal adsorption time was determined to be 2 h.

3.3. Study of the Evaporative Crystallization Process for Silver Nitrate

Evaporative crystallization is a critical step for obtaining high-purity silver nitrate crystals. The purified silver nitrate solution was heated in a water bath, and the supersaturation of the solution was increased by gradually evaporating the solvent, thereby driving the precipitation of silver nitrate crystals. The crystallization of silver nitrate follows the solution supersaturation–nucleation–growth mechanism: first, a supersaturated state is established, which then triggers nucleation, and finally, solute molecules orderly deposit on the crystal nucleus surface to achieve crystal growth. The impurity removal efficiency during the silver nitrate crystallization process is influenced by various process conditions, among which the crystallization yield and crystallization temperature are the most critical. The experimental results are shown in Figure 4.

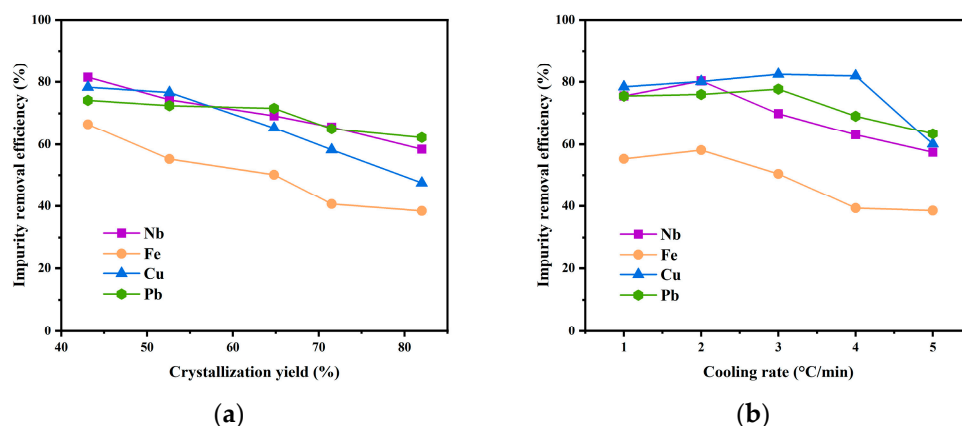


Figure 4. Crystallization step. (a) Crystallization yield; (b) cooling rate.

The effect of crystallization yield on impurity removal efficiency is shown in Figure 4a and Table S2. The crystallization yield was calculated according to the following equation:

Crystallization yield (%) = (Mass of AgNO_3 crystals obtained / Theoretical mass of AgNO_3 in the solution) $\times$ 100%.

As the crystallization yield increased, a pronounced downward trend was observed in the removal efficiency of impurity ions from the solution. When the crystallization yield exceeded 80%, the removal efficiency of some impurities had dropped to below 50%. The incorporation of impurities during crystallization was not caused by supersaturation-induced precipitation, but rather by crystal entrainment or lattice incorporation. As the crystallization yield increased, the amount of precipitated crystals grew, and the probability of impurity ions being entrapped into the solid phase increased, leading to a continuous decrease in impurity removal efficiency. Therefore, the crystallization yield should be controlled at approximately 65% to ensure both impurity removal effectiveness and process economics. At this yield, analysis of the mother liquor revealed impurity concentrations of Nb: 15.5 ppm, Fe: 12.4 ppm, Cu: 11.83 ppm, and Pb: 8.78 ppm, indicating that a significant fraction of the residual impurities were retained in the liquid phase rather than incorporated into the solid crystals. Silver losses during dissolution and impurity removal were negligible. The mother liquor was either further evaporated or recycled to the next batch for co-crystallization. The effect of cooling rate on impurity removal efficiency is shown in Figure 4b and Table S3. With the increase in cooling rate, the impurity removal efficiency first slowly increased and then sharply decreased, reaching a maximum at approximately 3 °C/h. Therefore, a cooling rate of 3 °C/h is recommended as the control parameter for the cooling process in practical production. From the perspective of crystallization kinetics, a faster cooling rate generates a higher degree of supercooling per unit time, resulting in stronger crystallization driving force, which leads to excessively rapid nucleation and crystal growth. Under such conditions, crystals grow insufficiently and develop a large number of lattice defects, onto which impurity ions readily adsorb, thereby reducing the impurity removal efficiency. Conversely, when the cooling rate is too low, the degree of supercooling is insufficient, and impurity ions have more time to incorporate into the crystals due to condensation effects, which is likewise detrimental to the removal of impurities [14–16].

All indicators of the high-purity silver nitrate product, prepared under the optimized process conditions (AC-1 dosage: 4 g/100 mL; adsorption temperature: 40 °C; adsorption time: 2 h; evaporative crystallization at 85 °C with cooling rate of 3 °C/h), were tested according to the Chinese national standard (GB/T 670-2007) [17]. The data indicates that all product indicators met the chemically pure grade standard (Table 2).

Table 2. National standard full test report of the high-purity silver nitrate crystals prepared under the optimized conditions.

Test Item	Index	Test Result	Conclusion
Content (AgNO_3), %	≥ 99.5	99.8	Qualified
Appearance	Colorless or white crystals	White crystals	Qualified
pH (50 g/L, 25 °C)	5.0–6.0	5.10	Qualified
Clarification test, No.	≤ 5	2	Qualified
Chloride (Cl), %	≤ 0.003	≤ 0.001	Qualified
Sulfate (SO_4), %	≤ 0.006	≤ 0.004	Qualified
Fe, %	≤ 0.0007	0.0004	Qualified
Cu, %	≤ 0.002	0.0002	Qualified
Pb, %	≤ 0.002	no detection	Qualified
Hydrochloric acid nonprecipitate, %	≤ 0.03	≤ 0.005	Qualified

3.4. Application Validation of Silver Nitrate in the Preparation of Photovoltaic Back Silver Powder

To validate the practical application performance of the high-purity silver nitrate prepared by the proposed process, photovoltaic back silver powders were synthesized under identical reduction conditions using two different silver sources: the unpurified silver nitrate solution and the high-purity silver nitrate solution purified by the combined impurity removal–crystallization process. The resulting silver powders were designated as YF-1 and YF-2. The micromorphology, tap density, and thermal behavior of the two silver powders were compared.

Figures 5 and 6 show the SEM images of YF-1 and YF-2, respectively. The surface of YF-1 was rough and densely covered with numerous fine particles. It exhibited a wide particle size distribution with an apparent mixture of large and small particles. In contrast, YF-2 displayed a smooth surface, good sphericity, and uniform particle size. The above morphological differences can be attributed to the effect of precursor purity on the growth process of silver crystallites. The trace impurities present in the unpurified solution interfered with the uniform nucleation and growth of silver crystallites during the liquid-phase reduction process, leading to abnormal growth of certain crystal facets or secondary nucleation, and resulting in the formation of a large number of fine particles. After deep purification, the interference from impurities was significantly suppressed, allowing the silver crystallites to grow uniformly, thereby yielding silver powder with a smooth surface and uniform particle size [18–20].

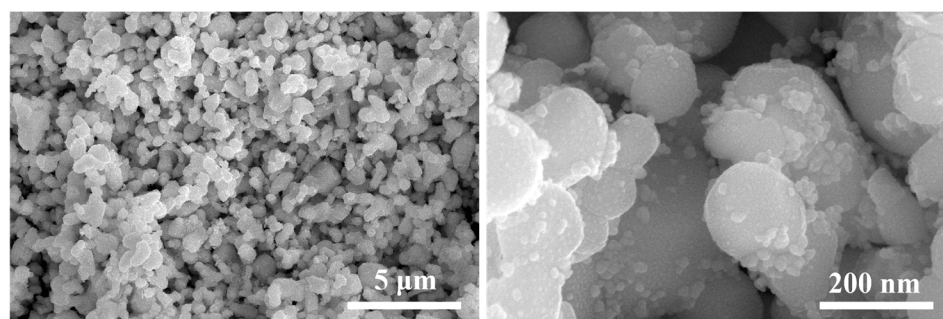
**Figure 5.** SEM image of YF-1.

Table 3 and Figure S3 present the relevant parameters of YF-1 and YF-2. The higher specific surface area of YF-2 ($9.9 \text{ m}^2 \text{ g}^{-1}$) compared with YF-1 ($6.1 \text{ m}^2 \text{ g}^{-1}$) is consistent with its finer particle size, given the inverse relationship between particle size and specific surface area. The tap density of YF-2 reached 3.4 g cm^{-3} , representing a 36% increase

compared with that of YF-1 (2.5 g cm^{-3}). Tap density is a key indicator for evaluating the packing performance of silver powder, and it is closely related to the packing morphology of the silver powder in the paste, sintering compactness, and interfacial bonding strength. Silver powder with a higher tap density packs more tightly, which facilitates the formation of a denser conductive network during sintering and increases the contact area between the silver layer and the substrate, thereby laying a structural foundation for favorable soldering adhesion [21,22]. It is noteworthy that YF-2 exhibited both a higher specific surface area and a higher tap density than YF-1. While these two parameters are typically inversely correlated, this apparent discrepancy can be explained by the dominant role of particle morphology. The higher specific surface area of YF-2 results from its finer particle size, whereas its higher tap density is attributed to its smooth spherical morphology and narrow particle size distribution, which enable more efficient particle packing. In contrast, the rough surface and irregular shape of YF-1 particles hinder close packing despite their lower specific surface area.

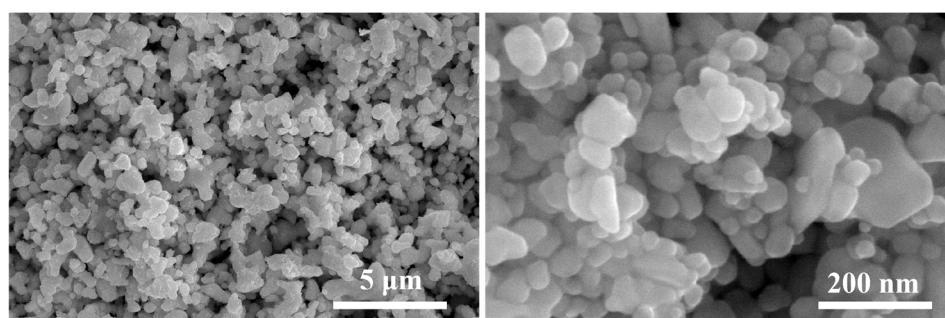


Figure 6. SEM image of YF-2.

Table 3. Comparison of parameters between YF-1 and YF-2.

Test Item	D_{50} (μm)	Mass Loss at 538°C	Tap Density (g cm^{-3})	Specific Surface Area ($\text{m}^2 \text{g}^{-1}$)
YF-1	0.20 ± 0.01	1.88%	2.5 ± 0.1	6.1
YF-2	0.18 ± 0.01	1.39%	3.4 ± 0.1	9.9

Figure 7 presents the TG-DSC curves of YF-1 and YF-2 measured in an air atmosphere. The thermal behavior can be divided into two distinct stages. In the first stage (room temperature to $\sim 300^\circ\text{C}$), both YF-1 and YF-2 exhibited a pronounced weight loss, accompanied by a sharp exothermic peak at approximately 300°C in the DSC curve. This weight loss is attributed to the oxidative decomposition and combustion of organic additives adsorbed on the silver powder surface during the reduction process. The greater weight loss observed for YF-1 in this stage indicates a higher content of residual organic additives. In the second stage ($\sim 300^\circ\text{C}$ to 538°C), the weight loss slowed significantly for both samples, suggesting the decomposition of residual carbonaceous species and strongly bound organic residues. At 538°C , the residual mass of YF-2 was 98.61%, higher than that of YF-1 (98.12%), confirming that the purified precursor yields silver powder with lower organic residue. The cleaner surface of YF-2 is attributed to its uniform particle morphology, which facilitates more effective removal of organic additives during the washing process. A lower organic residue is conducive to achieving a denser silver layer during sintering, further improving the conductivity and reliability of the electrode. It should be noted that the present study focuses on the purification process and silver powder characterization. Direct evaluation of paste printability, electrode sintering, and soldering adhesion is beyond the scope of this work and will be addressed in future research.

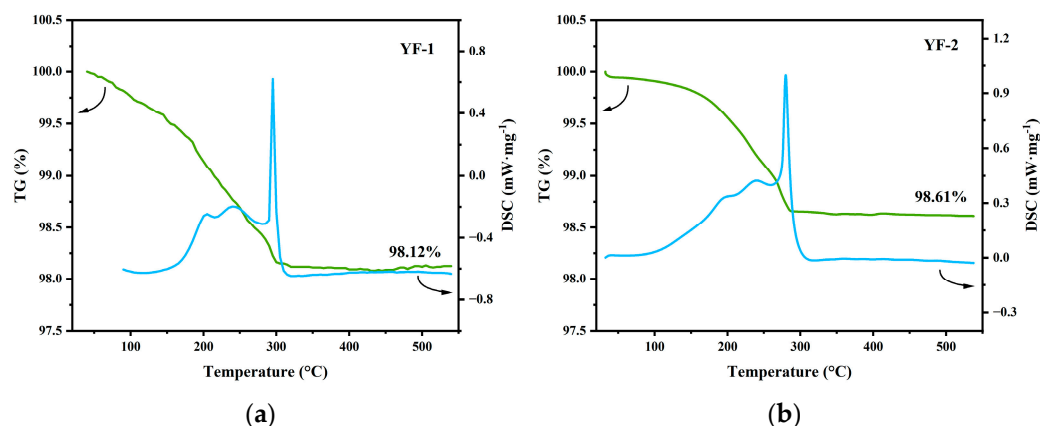


Figure 7. The TG-DSC curves of (a) YF-1 and (b) YF-2.

4. Conclusions

This study proposed a combined impurity removal–crystallization purification process to meet the purity requirements of high-purity silver nitrate for photovoltaic back silver paste. The main conclusions are as follows:

Impurity removal process optimization. Using self-made AC-1 as the adsorbent, the optimal process parameters were determined: an AC-1 dosage of 4 g/100 mL, an adsorption temperature of 40 °C, and an adsorption time of 2 h. Under these conditions, the contents of Nb, Fe, Cu, and Pb impurities in the crude silver nitrate solution decreased from the initial 44, 21, 16, and 12 ppm to below 4 ppm, respectively.

Crystallization process control. The evaporative crystallization step further removed impurities by regulating the crystallization yield and cooling rate, exploiting the partition difference of impurities between the solid and liquid phases. The impurity removal efficiency reached a maximum at a cooling rate of 3 °C/h, and the optimal crystallization yield was approximately 65%. The high-purity silver nitrate crystals prepared by the combined process met the chemically pure grade standard.

Application validation. The YF-2 silver powder synthesized using the high-purity silver nitrate as the silver source, compared with the unpurified sample YF-1, exhibited a smoother surface morphology, an increase in tap density from 2.5 g cm^{−3} to 3.4 g cm^{−3}, a narrowed particle size distribution, and a lower residual organic content. These improvements are attributed to the elimination of impurity interference in silver crystallite growth after precursor purification.

The combined impurity removal–crystallization process, through process optimization and quality control, achieved an enhancement in the chemical purity of silver nitrate, providing a reliable process control strategy for the industrial production of photovoltaic back silver powder. It should be noted that the present study focuses on silver powder characterization; comprehensive evaluations of paste printability, electrode sintering, soldering adhesion and solar cell performance will be pursued in future work.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr14152466/s1>, Figure S1: Silver oxide; Figure S2: By-product; Figure S3: XRD test of back silver; Figure S4: Particle size distribution curves of YF-1 and YF-2; Table S1: Experimental materials; Table S2: Final impurity concentrations in the silver nitrate crystals obtained under different crystallization yields; Table S3: Final impurity concentrations in the silver nitrate crystals obtained under different cooling rates.

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D.F.; writing—review and editing, D.F., J.Y., X.H. and H.S.; supervision, X.H.; project administration, H.S. All authors have read and agreed to the published version of the manuscript.

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