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Optimization of the experimental conditions for the synthesis of micro-size monodisperse spherical silver powders using Box–Behnken design

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ABSTRACT

Monodisperse and spherical micro-size silver powder, which has narrow size distribution and high purity, was prepared by using silver nitrate as metal source, L-ascorbic acid as reductant and sodium sulfate as dispersant. The aim of this paper was to study the simultaneous effects of pH (2–6), silver nitrate concentration [$AgNO_3$] (0.25–0.75 mol/L), dropping time t_d (5–15 min) and their interactions on properties of silver particles. In order to detect factor interactions and optimize these parameters, Box–Behnken design of experiments (a response surface methodology) was used. Synthesized silver powders were characterized by a laser particle size analyzer (LPSA), a scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). After surveying the experiment data and regression analysis of the data, a mathematical model was derived for optimizing particle size. The optimum condition was: [$AgNO_3$], 0.75 mol/L; pH, 6; and t_d, 5 min. The predicted particle size was 1.39 μm and the experimental particle size was 1.38 μm at the optimum condition, which showed that the model agreed well with the experimental data. It is found that the [$AgNO_3$] and dropping time have a positive effect and the pH value has a negative influence on the particle size. The possible mechanism for the formation of novel spherical silver particles is explored.

1. Introduction

Ultra-fine silver powders are widely used in the conductive silver paste due to their outstanding physical and chemical properties [1]. Preparation of micro-size spherical silver particles with good dispersion is a goal in fields such as silicon solar cell electronic paste, conductive silver paste, energy industry and conductive coating. Furthermore, spherical silver particle with a rough surface is highly active silver powder. It is widely applied in silver–zinc rechargeable batteries and catalysts. With the rapid development of the sintered paste, considerable interests in synthesizing silver powders have been ever-increased during the past years. There are a lot of preparation methods of silver powders, such as evaporation deposition, plasma approach, mechano-chemical approach, electrical explosion approach, micro-emulsion approach, chemical reduction and electrolytic deposition approach [2,3]. Among the preparation methods of silver powders, the liquid-phase reduction method is preferred due to the advantage of simple process flow, low environmental pollution and ease of control [4,5].

Liquid-phase reduction method has two steps including nucleation and growth. The key to obtaining desirable product is to alter the relative rates of nucleation and crystal growth. In our previous research [6], it was found that the pH value of the reaction solution, [$AgNO_3$], and dropping time t_d are the main factors influencing the particle size of silver powders. At the same time, the range of these parameters obtaining a minimum particle size (pH, 2–6; [$AgNO_3$], 0.25–0.75 mol/L; dropping time, 5–15 min) has been confirmed. However, the interactions among these factors could not be detected and the dynamic effect of various parameters on particle size could not be depicted.

In order to overcome above shortcomings, optimization study can be carried out using the response surface methodology (RSM). The Box–Behnken design (BBD), which is a common response surface method for experimental design, is very effective to evaluate the effects and interactions of process parameters on the process responses and optimize the synthesis procedure [7]. Furthermore, the experimental errors are minimized and the optimum conditions for synthesis procedure can be determined with a minimum number of experiments without the need for operating all possible experimental combinations by using the Box–Behnken design. RSM has been successfully applied for modeling and optimization in the metal powder preparation process [8,9].

The aim of this study was to optimize the synthesis procedure and establish a functional relationship between three process variables

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Table 1
Selected parameters and their levels.

Factor	Unit	Low (−1)	Center (0)	High (+1)
[$AgNO_3$]	mol/L	0.25	0.5	0.75
t_d	Min	5	10	15
pH	1	2	4	6

Table 2
Design of experiments and experimental and predicted results.

Standard order	Run order	[$AgNO_3$] (mol/L)	t_d (min)	pH	Particle size (μm) by experiment	Particle size (μm) by modeling
1	12	0.25	5	4	6.72	6.56
2	14	0.75	5	4	7.36	7.39
3	17	0.25	15	4	5.91	5.81
4	4	0.75	15	4	10.72	10.81
5	9	0.25	10	2	7.69	7.88
6	6	0.75	10	2	13.85	13.85
7	7	0.25	10	6	4.32	4.49
8	1	0.75	10	6	4.36	4.34
9	13	0.5	5	2	11.53	11.44
10	11	0.5	15	2	10.44	10.29
11	3	0.5	5	6	2.58	2.50
12	5	0.5	15	6	6.47	6.33
13	15	0.5	10	4	7.83	7.64
14	16	0.5	10	4	7.31	7.64
15	8	0.5	10	4	7.3	7.64
16	2	0.5	10	4	7.48	7.64
17	10	0.5	10	4	8.03	7.64

(pH value of reaction solution, silver nitrate concentration, dropping time) and the process response (particle size). Therefore, Box–Behken design of experiments (BBD) was applied to create a suitable mathematical model in terms of the particle size of the silver powders.

2. Experiment

2.1. Materials

Silver nitrate ($AgNO_3$, AR, Tongbai Xinhong Silver Products Co., Ltd, China), L-ascorbic acid ($C_6H_8O_6$, AR, Sinopharm Chemical Reagent Co., Ltd, China) and sodium sulfate (Na_2SO_4, AR, Sinopharm Chemical Reagent Co., Ltd, China) were used as the metal precursor, reducing agent and dispersant, respectively. Ethanol absolute (Tianjin Fengchuan Chemical Reagent Co., Ltd, China) and ammonia solution (NH_3, 25–28% wt., Tianjin Fengchuan Chemical Reagent Co., Ltd) are AR grade. Deionized water was homemade.

2.2. Synthesis

The specific experimental steps were described as follows: silver nitrate and ascorbic acid were dissolved in a certain amount of deionized water, respectively. The dispersant dosage ($Na_2SO_4/AgNO_3$ mass ratio) is 10%. Half of dispersant were added to silver nitrate and ascorbic acid solution as base solution and reducing solution, respectively. A certain concentration reducing solution was added into the specified amount of base solution with vigorous agitation for 0.5 h by a variable magnetic stirrer at 310 K. The pH value of mixture solution was controlled by adding a certain volume of ammonia solution. The as-prepared silver powder was filtrated and washed with deionized water and alcohol for three times, respectively, and then dried at 50 °C for 4 h.

2.3. Characterization

Powder morphology was observed by scanning electron microscopy (SEM, SPM-S3400N, Hitachi High-Technologies Corporation, Japan). The purity of the dried powder was characterized by X-ray diffraction (D/Max-2200, Rigaku Corporation, Japan) and EDS (SPM-S3400N, Hitachi High-Technologies Corporation, Japan). The average particle size and size distribution were studied by a laser particle size analyzer (OMEC LS900, Zhuhai OMEC Instrument Co., Ltd., China). Thermal characterization (TG and DSC) of silver powder was carried out with a NETZSCH STA 449F3 thermoanalyzer (NETZSCH Group, Germany) at a heating rate of 4 K/min under an N_2 atmosphere with a flow rate of 20 $cm^3 \cdot min^{-1}$.

2.4. Design of experiments (DOE)

Factors and their levels are shown in Table 1 and the experiments are shown in Table 2. The experiments were operated in random in order to ensure that the uncontrolled factors didn't influence the results [10]. The aim of this research was to obtain minimum micro-size silver particles. All the statistical analyses were carried out on the particle size.

Design of experiments and regression analysis of the experimental data were done by Design-Expert 8 (State-Ease, Inc.) software. To improve the precision of the model, 5 center point experiments were done. These points were added to the design to investigate the random error of the experiments [11], the nonlinearity and reproducibility and

Table 4
The choice and comparison of model.

Sum of source	Mean squares	Degree of freedom	Mean square	*F* value	*p*-value Prob > *F*	
Mean vs total	992.59	1	992.59			
Linear vs mean	103.62	3	34.54	21.89	<0.0001	
2FI vs linear	19.91	3	6.64	109.83	<0.0001	Suggested
Quadratic vs 2FI	0.1	3	0.033	0.46	0.7175	
Cubic vs quadratic	0.079	3	0.026	0.25	0.8606	Aliased
Residual error	0.43	4	0.11			
Total	1116.72	17	65.69			

Table 3
ANOVA results.

Source	Sum of squares	Degree of freedom	Mean square	*F* value	*p*-value Prob > *F*	
Model	123.53	6	20.59	340.71	<0.0001	Significant
A-[$AgNO_3$]	16.97	1	16.97	280.75	<0.0001	
B-t_d	3.58	1	3.58	59.21	<0.0001	
C-pH	83.08	1	83.08	1374.80	<0.0001	
AB	4.35	1	4.35	71.94	<0.0001	
AC	9.36	1	9.36	154.96	<0.0001	
BC	6.20	1	6.20	102.60	<0.0001	
Residual error	0.60	10	0.06			
Lack of fit	0.18	6	0.03	0.28	0.9198	Not significant
Pure error	0.43	4	0.11			
Cor total	124.13	16				
R^2: 0.9951	Adjusted R^2: 0.9922		Predicted R^2: 0.9892		Adeq precision: 71.922	