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Significant Parameters in the Optimization of Synthesis of Silver Nanoparticles by Chemical Reduction Method

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Silver nanoparticles of narrow size distributions were synthesized by reduction of highly concentrated silver nitrate ($AgNO_3$) solution with sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) in the presence of polyvinyl pyrrolidone (PVP). An orthogonal experimental design (OED) with L_9 orthogonal array was employed as a chemometric method to optimize the experimental conditions for the synthesis of silver nanoparticles. Particle size of silver nanoparticles was considered as the defining characteristics. The concentration of reducing agent, weight ratio of $AgNO_3$ to protecting agent, and temperature were optimized using a three-level OED and nine experiments. The particle size was characterized to optimize the synthesis conditions. The concentration of reducing agent emerged as the most important parameter influencing the particle size. The temperature also influenced the particle size. Based on 1 M $AgNO_3$ solution and 0.1 M $NaH_2PO_2 \cdot H_2O$, 1.7 g silver nanoparticles of 10-50 nm were obtained from 3.4 g silver nitrate with weight ratio of PVP/$AgNO_3$ equal to unity at 40 °C.

Keywords chemical reduction, orthogonal design, silver nanoparticles

1. Introduction

Metal nanoparticles, such as those of silver and gold, have attracted much attention in recent years due to their properties (Ref 1). Silver nanoparticles in particular show enhanced catalytic activity, high electrical conductivity, bactericidal action, and unique optical properties. They are used in a variety of applications such as catalysis, photonics, biological fields, conductive inks, thick film pastes, and adhesives for various electronic components (Ref 2-5). Therefore, much effort has focused on producing silver nanoparticles with controlled size, shape, and size distribution.

Many methods have been applied to synthesize silver nanoparticles, such as chemical reduction (Ref 6-8), photochemical or radiation-chemical reduction (Ref 9, 10), metallic wire explosion (Ref 11), sonochemical method (Ref 12) and plasma method (Ref 13). From a practical point of view, chemical reduction from aqueous solutions is the preferred approach to obtain nano-sized silver particles. However, the procedures developed to yield stable silver dispersions at low concentration of silver ions are not suitable for large-scale manufacturing (Ref 14). In the formation of silver nanoparticles by chemical reduction method, the properties of nanoparticles are affected by parameters such as concentration of reducing agent, weigh ratio of $AgNO_3$ to protecting agent, and temperature. The interrelationships between these parameters are complex, and efforts to analyze chemical reduction systems require excessive work (Ref 15). Hence, conventional experimental methods are inefficient for providing enough information to study such interrelationships.

The precipitation process, described here, yields highly concentrated silver ion solution of 1.0 M. An orthogonal experimental design is introduced in this paper. Orthogonal design is an analysis tool that enables many parameters to be considered in one experiment with a minimal number of observations. Full factorial experiments can require many runs, and a carefully chosen fraction of runs may be all that is necessary. Orthogonal design is a combination of mathematical and statistical techniques used in empirical studies to economically characterize a complicated process. It requires fewer experiments to study all levels of all input parameters and filters out some effects due to statistical variation (Ref 16). The results of orthogonal design are analyzed by means of apparent analytical methods which can determine the optimum experimental conditions for the synthesis of silver nanoparticles. Apparent analytical method can also yield insight into the effects of parameter interactions that are not evident when considering only one parameter at a time.

The objective of the present study is to yield relatively large volumes and stable dispersions of silver nanoparticles in a simple and cost-effective manner by reduction of concentrated aqueous solutions of silver nitrate. Optimal synthesis conditions were obtained by implementing orthogonal design.

2. Experimental Procedure

2.1 Materials and Methods

All chemicals used in the experiment were analytic reagents (AR). Silver nitrate ($AgNO_3$, 99.8%) was provided by Shanghai institute of fine chemical materials. Sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) and sodium hexametaphosphate ($(NaPO_3)_6$) were purchased from Tianjin Chenfu Chemical Reagent Corp.

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Table 1 Factors and levels used in this experiment

Level	Factor A [$NaH_2PO_2 \cdot H_2O$], mol/L	Factor B PVP/$AgNO_3$ weight ratio	Factor C Temperature, °C
1	0.05	0.74:1	30
2	0.1	1:1	40
3	0.2	1.5:1	50

Polyvinyl pyrrolidone (PVP) was obtained from China Medicine (Group) Shanghai Chemical Reagent Corp. Benzotriazole ($C_6H_5N_3$) was purchased from Hunan Huihong Reagent Corp. In this study, sodium hypophosphite, polyvinyl pyrrolidone, and sodium hexametaphosphate were used as reducing agent, protecting agent, and dispersant, respectively. In addition, benzotriazole and distilled water were used as washing agents.

2.2 Preparation of Silver Particles

The experimental investigation was carried out under atmospheric pressure using silver nitrate solution of 1.0 M as the precursor with vigorous stirring by a magnetic stirrer. The oxidation solution (OS) was prepared by adding 3.4 g of $AgNO_3$ into 20 mL distilled water. The reducing solution (RS) was prepared by dissolving PVP, $NaH_2PO_2 \cdot H_2O$, and $(NaPO_3)_6$ into distilled water together, and the pH of RS was adjusted to 2 using dilute sulfuric acid. RS was heated to 40 °C while stirring and OS was added into RS dropwise. The mixed solution was stirred further for 30 min. The precipitated silver particles were separated in a centrifuge at 7000 rpm for 10 min. The solid products were collected and washed with benzotriazole (wt = 1.0%), acetone and ethanol. They were then dried under vacuum at 60 °C for 6 h.

2.3 Characterization

The synthesized particles were characterized using different techniques.

The transmission electron microscopy (TEM) measurements were taken with a Jeol electron microscope (Model Tecnai $G^2$20). The samples for observation were suspended in ethanol and allowed to settle for some time. Then, two drops of the supernatant dispersion were placed onto a carbon film supported by a copper grid.

The x-ray diffraction (XRD) data on the samples were taken with Cu Kα radiation (λ = 1.54 Å) on a powder diffractometer operated in 20-80° (2θ) range. Samples were prepared as uniform thin films supported on the slides.

The Fourier Transform Infrared (FT-IR) spectra of the samples were obtained in an AVATR360 spectrophotometer in the 4000-400 cm^{-1} range. The samples were prepared into KBr pellets.

2.4 Orthogonal Design and Experimental Parameters

Three parameters that could affect the particle size were chosen. Table 1 shows the parameters and their levels. The orthogonal array of L_9 type was used and is represented in Table 2. L and subscript 9 mean Latin square and the repetition number of the experiment, respectively. Four three-level parameters can be positioned in a L_9 orthogonal array table. One column of the orthogonal array was assigned as error term to increase the integrality of the array and the accuracy of the analyses. The numbers 1, 2, and 3 in Table 2 indicate the first, second, and third levels of a parameter, respectively.

Table 2 Orthogonal array table of L_9 and experimental measured values for silver particle size

Run no.	A	B	C	Error	Average particle size, nm
1	1	1	1	1	15
2	1	2	2	2	25
3	1	3	3	3	35
4	2	1	2	3	30
5	2	2	3	1	35
6	2	3	1	2	55
7	3	1	3	2	85
8	3	2	1	3	32
9	3	3	2	1	35

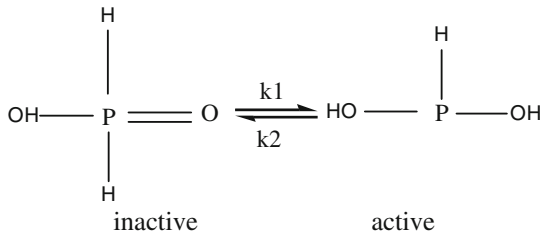

Fig. 1 The transformation of the hypophosphite

3. Results and Discussion

3.1 Effect of pH and Possible Reaction Mechanism

The reaction rates are remarkably affected by the pH of the solution. The reducing power of sodium hypophosphite is poor at the high pH of the reaction medium. A lower pH is favored for higher reducing power. This phenomenon can be explained as follows (Ref 17): hypophosphite was changed from normal structure (inactive type) to active structure (metastable structure with two hydroxyls) in acidic pH solution (Fig. 1). However, when the pH of the solution was too low, silver mirror phenomenon occurred on the container wall. Based on experiments, the pH of the solution was kept at 2 throughout this study.

The possible stoichiometric reaction between hypophosphite and silver ion in an acidic pH solution can be written as follows:

$$Ag^+ + PVP \rightarrow Ag(PVP)^+ \quad \text{(Eq 1)}$$

$$4[Ag(PVP)]^+ + H_2PO_2^- + 2OH^- \rightarrow 4Ag(PVP) \downarrow + H_2PO_4^- + 2H^+ \quad \text{(Eq 2)}$$

As described in Eq 1 and 2, Ag^+ was compounded with PVP and complex ions were generated. The hypophosphite ion then reduces silver ions to silver atom. The relative mole ratio of hypophosphite to silver was actually kept at 4 throughout this study. This ratio should be sufficient to reduce all silver ions in the solution.

Table 3 Results of the main effect for each variable on the size of the silver nanoparticles

	Mean size of silver nanoparticles, nm			
Factors	**Level 1**	**Level 2**	**Level 3**	**Maximum-minimum**
A	25	40	51	26
B	43	31	42	12
C	34	30	52	22

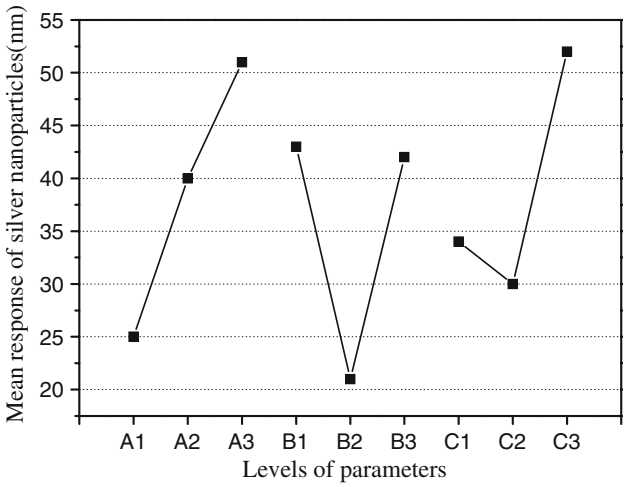

Fig. 2 The main effects plot for each parameter

3.2 Data Analysis

An orthogonal design array was used to identify the optimal conditions and to select the parameters having a major influence on the particle size of silver nanoparticles. Nine experiments were performed to estimate the best conditions for the synthesis of silver nanoparticles. The structure of orthogonal design and the results of measurement are shown in Table 2 and the smallest value of particle size (15 nm) is shown in run no. 1. This value means that silver nanoparticles having an average size of 15 nm were synthesized. The samples were mainly characterized for their particle size using TEM.

The data obtained by performing experiments were analyzed by means of apparent analytical method to calculate the main effects for each variable parameter. Apparent analytical method uses the mean value to measure the quality characteristic. Since the experimental design is orthogonal, it is possible to separate the effect of each parameter at different levels. For example, the mean particle size for [$NaH_2PO_2 \cdot H_2O$] at levels 1, 2, and 3 can be calculated by averaging the average particle size for the experiments 1-3, 4-6, and 7-9, respectively. The mean particle size for each level of the other parameters can be computed in a similar manner.

The mean particle size at each level of the parameters is summarized and the value response for particle size is shown in Table 3. The maximum-minimum values of $NaH_2PO_2 \cdot H_2O$ concentration are the highest values. Therefore, $NaH_2PO_2 \cdot H_2O$ concentration is the significant parameter affecting the particle size. The next parameter is temperature and the last one is PVP/$AgNO_3$ weight ratio. It was also found that the values

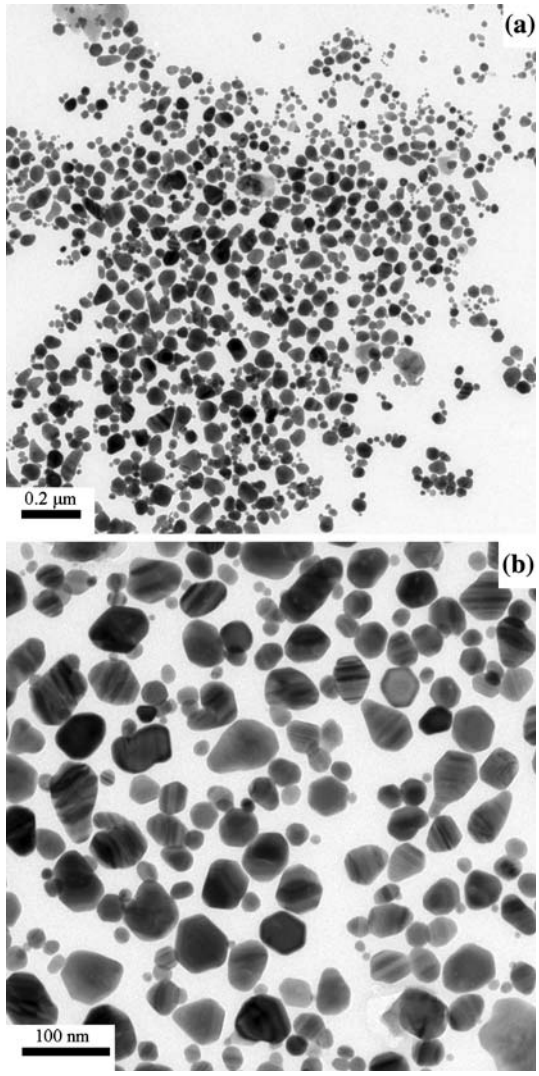

Fig. 3 Transmission electron micrographs of silver nanoparticles under the optimal conditions

(maximum-minimum) of A (concentration of $NaH_2PO_2 \cdot H_2O$) and C (temperature) are much higher than any other factors, implying that these two parameters most significantly influence the synthesis of silver nanoparticles. In a factorial analysis, mean plots are used to represent the data and provide a first look at the parameter effects. Figure 2 shows the plot of the overall means of each parameter for all the data collected. The average particle size is considered as the characteristic parameter to determine the optimal conditions. To obtain optimal conditions, the lower the level of a parameter, the better it is to achieve optimal conditions. At the same time, the size distribution of silver nanoparticles and reaction rate were also evaluated. The optimum conditions for the synthesis of silver nanoparticles are A2, B2, and C2. In other words, the optimal parameters for silver nanoparticles are A at level 2, B at level 2, and C at level 2.

The use of PVP has two purposes: one is to generate a complex compound with the silver ion, and control the reaction process as discussed in Sect 3.1, and the other is to protect particles from growth and agglomeration (Ref 18). When the amount of PVP is not enough, it cannot form a complete protection layer, and the particles will agglomerate easily. With

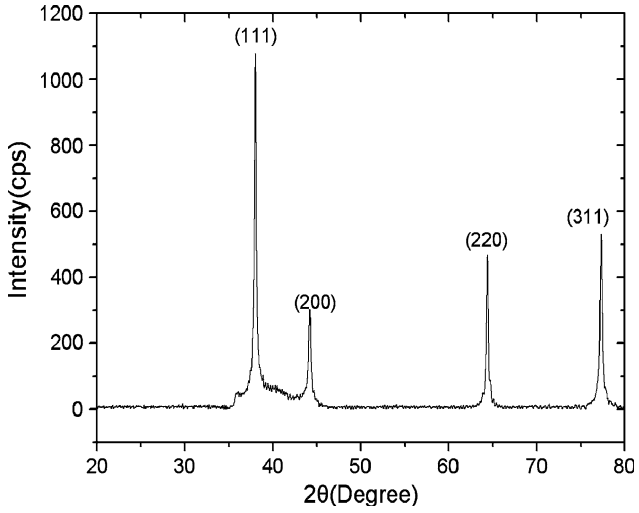

Fig. 4 The XRD spectrum of the silver nanoparticles

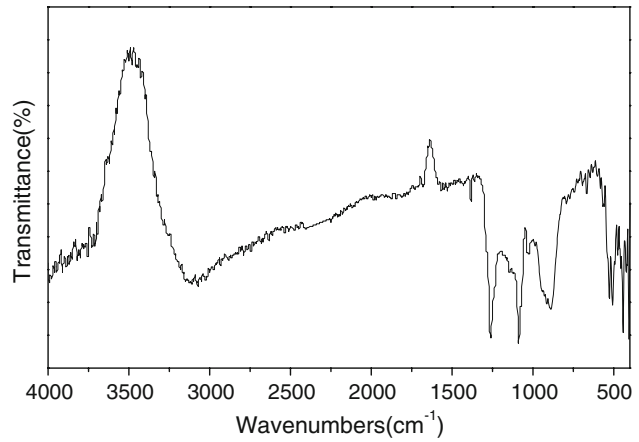

Fig. 5 FT-IR spectra of the silver nanoparticles

more disperser added, it can form a more perfect layer quickly, and the layer protects the particles from agglomeration and growth.

3.3 Characterization of Silver Nanoparticles

The TEM micrograph of the silver nanoparticles obtained at optimal conditions is shown in Fig. 3. As shown in Fig. 3(a) and (b), well-dispersed silver nanoparticles with quasi-spherical shape were synthesized, and the diameters of silver nanoparticles ranged from 10 to 50 nm.

Representative XRD analysis is reported in Fig. 4. It indicates that the particles are silver and well crystallized showing sharp peaks of (111), (200), (220), and (311). This reveals that the resultant particles are pure face-centered cubic (fcc) silver.

The FT-IR spectra of silver nanoparticles are shown in Fig. 5. The FT-IR measurement shows a peak at 3073 cm^{-1} for the characteristic C-H stretching vibration of CH_2. The peak at 1260 cm^{-1} can be attributed to the absorption band of C-N stretching vibration. It clearly indicates that the protecting agent adsorbs on the surface of silver particles. All characteristic bands of metal oxides are present between 400 and 1100 cm^{-1}.

4. Conclusions

Silver nanoparticles have been cost-effectively synthesized by reduction of high-concentration silver nitrate with sodium hypophosphite in the presence of PVP as protecting agent in an acidic pH solution. An orthogonal experimental design was introduced to optimize the parameter values for obtaining desired characteristics, since it could improve the repeatability and quantitative capabilities to synthesize silver nanoparticles. Various parameters affecting the particle size were analyzed and the synthesis conditions were optimized by means of apparent analytical method. As a result, the concentration of reducing agent and the temperature were identified as the main parameters affecting the particle size. Under optimal conditions, well-dispersed silver nanoparticles in the size range 10-50 nm and quasi-spherical shape were synthesized. The nanoparticles were pure face-centered cubic silver.

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